

Background Document I:

Chemical Neutralization as a Land Disposal Restriction Treatment Technology for Chemical Agent Associated Waste

Utah Chemical Agent Rule (UCAR)

May 1999

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**CHEMICAL NEUTRALIZATION AS A
LAND DISPOSAL RESTRICTION TREATMENT TECHNOLOGY
FOR CHEMICAL AGENT ASSOCIATED WASTE**

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CONTENTS

NOTATION	ix
EXECUTIVE SUMMARY	S-1
1 INTRODUCTION.....	1-1
1.1 Regulatory Background of Chemical Neutralization as an Applicable Treatment Technology for Land Disposal Restrictions	1-1
1.2 Purpose and Scope	1-2
1.3 Report Organization	1-3
2 INDUSTRY AFFECTED AND WASTE CHARACTERIZATION.....	2-1
2.1 Industry Affected and Process Descriptions	2-1
2.1.1 Dugway Proving Ground	2-1
2.1.2 Deseret Chemical Depot.....	2-1
2.1.3 Chemical Agent Munitions Disposal System.....	2-2
2.1.4 Tooele Chemical Destruction Facility.....	2-4
2.2 Chemical Agent Characterization and Chemical Neutralization Solutions	2-7
2.2.1 Properties and Reactions of Chemical Agents under Neutralization Conditions	2-7
2.2.2 Chemical Neutralization Solutions	2-37
3 SUPPORT FOR CHEMICAL NEUTRALIZATION OF CHEMICAL AGENT WASTE STREAMS AS APPLICABLE AND DEMONSTRATED TREATMENT TECHNOLOGIES	3-1
3.1 Applicability of Chemical Neutralization as a Treatment Technology.....	3-1
3.1.1 Chemical Neutralization of GB by Alkaline Hydrolysis	3-4
3.1.2 Chemical Neutralization of GB with Hypochlorite.....	3-5
3.1.3 Chemical Neutralization of GA by Alkaline Hydrolysis	3-6
3.1.4 Chemical Neutralization of GA with Hypochlorite	3-8
3.1.5 Chemical Neutralization of GD by Alkaline Hydrolysis	3-9
3.1.6 Chemical Neutralization of GD with Hypochlorite	3-10
3.1.7 Chemical Neutralization of TGD.....	3-11
3.1.8 Chemical Neutralization of GF by Alkaline Hydrolysis.....	3-11
3.1.9 Chemical Neutralization of GF with Hypochlorite	3-12
3.1.10 Chemical Neutralization of VX by Alkaline Hydrolysis	3-14
3.1.11 Chemical Neutralization of VX with Hypochlorite in Basic Solution.....	3-14
3.1.12 Chemical Neutralization of Vx by Alkaline Hydrolysis	3-16
3.1.13 Chemical Neutralization of Vx with Hypochlorite in Basic Solution.....	3-16
3.1.14 Chemical Neutralization of H/HD with Hypochlorite in Basic Solution.....	3-18
3.1.15 Chemical Neutralization of HT with Hypochlorite in Basic Solution	3-18
3.1.16 Chemical Neutralization of HQ with Hypochlorite in Basic Solution.....	3-19

CONTENTS (Cont.)

3.1.17 Chemical Neutralization of HN1 and HN3 with Hypochlorite in Basic Solution	3-20
3.1.18 Chemical Neutralization of L with Hypochlorite in Basic Solution	3-20
3.1.19 Chemical Neutralization of HL with Hypochlorite in Basic Solution	3-21
3.1.20 Applicability of Chemical Neutralization as a Treatment Technology for Chemical Agent Related Waste Streams	3-22
3.2 Performance Database	3-22
4 SUMMARY AND CONCLUSIONS	4-1
5 REFERENCES	5-1
APPENDIX A: Chemical Structures Dictionary	A-1

TABLES

2.1 DPG Chemical Agent Related Waste Streams and Chemical Neutralization Status	2-2
2.2 DCD Chemical Agent Related Waste Streams and Chemical Neutralization Status	2-3
2.3 CAMDS Chemical Agent Related Waste Streams and Chemical Neutralization Status	2-5
2.4 TOCDF Chemical Agent Related Waste Streams and Chemical Neutralization Status	2-6
2.5 Chemical Agents by Location	2-8
2.6 Chemical Neutralization Solutions Used at DPG	2-8
2.7 Chemical Neutralization Solutions Used at DCD	2-9
2.8 Chemical Neutralization Solutions Used at CAMDS	2-9
2.9 Chemical Neutralization Solutions Used at TOCDF	2-9
2.10 Nerve Agent Substituents	2-11
2.11 Half-Lives of Nerve Agents	2-13

TABLES (Cont.)

2.12 Quantity of Chemical Agent Remaining after the Specified Number of Half-Lives.....	2-14
2.13 Environmentally Relevant Properties of GB.....	2-16
2.14 Environmentally Relevant Properties of GA	2-18
2.15 Environmentally Relevant Properties of GD	2-20
2.16 Environmentally Relevant Properties of GF	2-22
2.17 Environmentally Relevant Properties of VX	2-24
2.18 Environmentally Relevant Properties of Vx	2-26
2.19 Environmentally Relevant Properties of HD	2-29
2.20 Environmentally Relevant Properties of HT	2-31
2.21 Environmentally Relevant Properties of HQ	2-32
2.22 Environmentally Relevant Properties of L.....	2-33
2.23 Environmentally Relevant Properties of HL.....	2-35
2.24 Environmentally Relevant Properties of HN1	2-36
2.25 Environmentally Relevant Properties of HN3	2-38
2.26 Approximate pH Values of Solutions of Various Concentrations of Selected Bases.....	2-39
3.1 Thermochemical and Kinetic Data.....	3-3
3.2 Products of Alkaline Hydrolysis of GB	3-5
3.3 Products of Alkaline Hydrolysis of GB in Sodium Hypochlorite Solution	3-6
3.4 Products of Hydrolysis of GA in Sodium Hydroxide	3-7
3.5 Reaction of GA with Sodium Hypochlorite.....	3-8
3.6 Products of Alkaline Hydrolysis of GD	3-10

TABLES (Cont.)

3.7	Products of Alkaline Hydrolysis of GD in Sodium Hypochlorite Solution	3-11
3.8	Products of Alkaline Hydrolysis of GF.....	3-12
3.9	Products of Alkaline Hydrolysis of GF in Sodium Hypochlorite Solution	3-13
3.10	Products of Alkaline Hydrolysis of VX	3-15
3.11	Products of Neutralization of VX in Sodium Hypochlorite Solution	3-16
3.12	Products of Alkaline Hydrolysis of Vx.....	3-17
3.13	Products of Neutralization of Vx in Sodium Hypochlorite Solution	3-17
3.14	Products of Neutralization of H/HD in Sodium Hypochlorite Solution	3-19
3.15	Products of Neutralization of L in Sodium Hypochlorite Solution.....	3-21
3.16	DPG Performance Database.....	3-23
3.17	DCD Performance Database	3-26
3.18	CAMDS Performance Database.....	3-29
3.19	TOCDF Performance Database.....	3-30
4.1	Recommendation Summary	4-1
4.2	Alkaline Hydrolysis of GA	4-2
4.3	Alkaline Hypochlorite Neutralization of GA	4-2
4.4	Alkaline Hydrolysis of GB.....	4-3
4.5	Alkaline Hypochlorite Neutralization of GB	4-3
4.6	Alkaline Hydrolysis of GD	4-4
4.7	Alkaline Hypochlorite Neutralization of GD	4-4
4.8	Alkaline Hydrolysis of GF	4-5
4.9	Alkaline Hypochlorite Neutralization of GF.....	4-5

TABLES (Cont.)

4.10 Alkaline Hydrolysis of VX	4-6
4.11 Alkaline Hypochlorite Neutralization of VX	4-6
4.12 Alkaline Hydrolysis of Vx	4-7
4.13 Alkaline Hypochlorite Neutralization of Vx.....	4-7
4.14 Alkaline Hypochlorite Neutralization of H/HD	4-8
4.15 Alkaline Hypochlorite Neutralization of HT	4-8
4.16 Alkaline Hypochlorite Neutralization of HQ	4-9
4.17 Hypochlorite Neutralization of HN1 and HN3	4-9
4.18 Alkaline Hypochlorite Neutralization of L	4-10
4.19 Alkaline Hypochlorite Neutralization of HL	4-10

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NOTATION

Army	U.S. Army
AsO ₃	arsenic trioxide
AsCl ₃	arsenic trichloride
atm-m ³ /mol	atmosphere-cubic meter(s) per mole
°C	degrees Celsius
cal/g	calories per gram
cal/mole	calories per mole
CAMDS	Chemical Agent and Munitions Disposal System
Ca(OCl) ₂	calcium hypochlorite (HTH)
CaCl(OCl)	calcium chloride hypochlorite (STB)
CaO	calcium oxide
CAS Req. No.	Chemical Abstracts Service Registry Number
CH-TG	mustard chlorohydrin-thiodiglycol complex
ClO ₃ ⁻	chlorate ion
cm ² /s	square centimeter(s) per second
CVAA	2-chlorovinylarsonous acid
DCD	Deseret Chemical Depot
DESH	2-diisopropylaminoethanethiol
DFS	deactivation furnace system
DIMP	diisopropylmethylphosphonate
DPE	demilitarization protective ensemble
DPG	Dugway Proving Ground
DSHW	Division of Solid and Hazardous Waste (State of Utah)
EA2192	S-(2-diisopropylaminoethyl) methylphosphonothioic acid
EA4196	bis(2-diisopropylaminoethyl) disulfide
EMPA	ethyl methylphosphonic acid
EPA	U.S. Environmental Protection Agency
EtOH	ethanol
F ⁻	fluoride ion
ΔG	change in free energy
g/cc	gram(s) per cubic centiliter
g/cm ³	gram(s) per cubic centimeter
g/L	gram(s) per liter
g/mL	gram(s) per milliliter
g/mol	gram(s) per mole
GA	tabun
GB	sarin

GD	soman
GF	cyclohexyl methylphosphonofluoridate
ΔH	heat of reaction
h	hour(s)
H	levinsein mustard; sulfur mustard
HCN	hydrogen cyanide
HD	distilled levinsein mustard; distilled sulfur mustard
HF	hydrogen fluoride
HL	distilled levinsein mustard - lewisite mixture
HN1	2,2'-dichlorotriethylamine; nitrogen mustard
HN2	2,2'-dichlorotriethylmethylanine; nitrogen mustard
HN3	2,2',2"-trichlorotriethylamine; nitrogen mustard
H ₂ O	water
HQ	75% HD/25% 1,2-bis(2-chloroethylthio) ethane mixture
HT	distilled levinsein mustard [bis-(2-chloroethylthio)]ethyl ether mixture
HTH	high-test hypochlorite (calcium hypochlorite)
H-TG	mustard thiodiglycol complex
H-2TG	mustard bis(thiodiglycol) complex
IMPA	isopropyl methylphosphonic acid
K	kelvin
K _a	acid dissociation constant
kcal/mol	kilocalorie(s) per mole
K _{eq}	equilibrium constant
K _H	Henry's Law constant
K _{oc}	soil organic carbon/water partition
K _{ow}	octanol/water partition coefficient
L	lewisite
L1	2-chlororovinylchloroarsine
L2	bis-(2-chlorovinyl)chloroarsine
L3	tris-(2-chlorovinyl)arsine
LDR	Land Disposal Restriction
LDRUG	Land Disposal Restrictions Utah Group
LIC	liquid incinerator
M	mole(s)
mg/L	milligram(s) per liter
mg/m ³	milligram(s) per cubic meter
min	minute(s)
mm Hg	millimeter(s) of mercury
MPA	methylphosphonic acid
MPF	metal parts furnace

NaCN	sodium cyanide
Na ₂ CO ₃	sodium carbonate
Na[EMPA]	sodium salt of ethyl methylphosphonic acid
NaF	sodium fluoride
Na[IMPA]	sodium salt of isopropyl methylphosphonic acid
NaOCl	sodium hypochlorite
NaOH	sodium hydroxide
Na[PMPA]	sodium salt of pinacolyl methylphosphonic acid
NH ₄ OH	ammonia
NMR	nuclear magnetic resonance spectroscopy
OCI ⁻	hypochlorite ion
OH ⁻	hydroxide ion
PAS	pollution abatement system
pK _a	negative logarithm of K _a (acid dissociation constant)
PMPA	pinacolyl methylphosphonic acid
Q	1,2-bis(2-chloroethylthio)ethane
RCRA	Resource Conservation and Recovery Act
RD&D	research, development, and demonstration
RHA	Residue Handling Area
ΔS	change in entropy
S _N 2	second-order nucleophilic substitution
s	second(s)
SBCCOM	Soldier and Biological Chemical Command (U.S. Army)
STB	supertropical bleach
TGD	thickened soman
TOCDF	Tooele Chemical Destruction Facility
TSDF	treatment, storage, and disposal facility
μg/L	microgram(s) per liter
UCAR	Utah Chemical Agent Rule
VX	O-ethyl S-(2-diisopropylaminoethyl) methylphosphonothioate
Vx	S-2(2-diethylamino)ethyl O-isobutyl methylphosphonothioate

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CHEMICAL NEUTRALIZATION AS A LAND DISPOSAL RESTRICTION TREATMENT TECHNOLOGY FOR CHEMICAL AGENT ASSOCIATED WASTE

EXECUTIVE SUMMARY

The purpose of this document is to support the Utah Department of Environmental Quality, Division of Solid and Hazardous Waste (DSHW) in developing land disposal restriction (LDR) treatment standards for chemical agents and associated wastes. It was developed under the direction of the Land Disposal Restrictions – Utah Group (LDRUG) that was established by the U.S. Army Soldier and Biological Chemical Command, Aberdeen Proving Ground, Maryland. The LDRs were mandated for hazardous wastes by the 1984 Hazardous and Solid Waste Amendments to the Resource Conservation and Recovery Act (RCRA). The State of Utah has been authorized by the U.S. Environmental Protection Agency (EPA) to operate the RCRA program within the state and has adopted EPA's RCRA characteristics and lists of hazardous wastes. Because the Deseret Chemical Depot (DCD) and the Dugway Proving Ground (DPG) have missions associated with chemical agents that were not listed by EPA, the DSHW added chemical agents and associated wastes within the state in July 1988. At that time, no management standards, such as LDR treatment standards, were developed. In 1995, the USDHW announced a regulatory initiative to establish LDR treatment standards as part of the Utah Chemical Agent Rule (UCAR).

This document assesses the ability of chemical neutralization to treat the various chemical agent waste streams to or below the LDR concentration standards that are to be established in the UCAR. The document contains information concerning types and locations of the chemical agents and associated waste streams, chemical agent properties and reactions, a description of processes and chemical neutralization solutions, and expected reaction products. Data are presented that were used to determine if the chemical neutralization procedures are "applicable" and can be considered "demonstrated." Of the 18 procedures evaluated, 15 were found to be "applicable" and "demonstrated" and are recommended as LDR treatment standards. Two of the procedures are not preferred because of the formation of undesirable by-products and, therefore, are not recommended. Basic data on one procedure, the chemical neutralization of HN1 and HN3, are lacking to determine whether it is "applicable," and it has not been "demonstrated."

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1 INTRODUCTION

This report was prepared by the Land Disposal Restrictions – Utah Group (LDRUG) established by the U.S. Army Soldier and Biological Chemical Command (SBCCOM). This report is intended as a background document to support the Utah Department of Environmental Quality, Division of Solid and Hazardous Waste (DSHW) in developing Land Disposal Restriction (LDR) treatment standards for chemical agents and associated wastes. This report summarizes the literature and presents a performance database to support chemical agent related waste stream chemical neutralization as a specific LDR technology.

AGEISS Environmental, Inc., Denver, Colorado, and Analytical Quality Solutions, South Weber, Utah, assembled and analyzed the background information and prepared the initial report on the Dugway Proving Ground (DPG) waste stream chemical neutralization as a treatment technology (AGEISS 1998). Information from the initial DPG report was combined with information on chemical neutralization operations at the Deseret Chemical Depot (DCD), Tooele Chemical Destruction Facility (TOCDF), and Chemical Agent Munitions Disposal System (CAMDS) to prepare this report.

1.1 REGULATORY BACKGROUND OF CHEMICAL NEUTRALIZATION AS AN APPLICABLE TREATMENT TECHNOLOGY FOR LAND DISPOSAL RESTRICTIONS

The LDRs were mandated for wastes designated as hazardous under the Federal Resource Conservation and Recovery Act (RCRA) program by the 1984 Hazardous and Solid Waste Amendments to RCRA. LDRs are treatment requirements for wastes before land disposal. When a waste is determined to be hazardous, it must be treated to comply with specified treatment standards prior to land disposal. These treatment standards substantially diminish the toxicity of the waste or substantially reduce the likelihood of migration of hazardous constituents from the waste (RCRA Section 3004(m)).

RCRA was intended by Congress to be a state-implemented program. The U.S. Environmental Protection Agency (EPA) was charged with developing a minimum set of standards for managing hazardous waste under the RCRA program; states would then adopt these regulations and seek authorization from EPA to implement the RCRA program within their boundaries. States cannot be less stringent or broader in scope than the federal program in adopting EPA's regulations; however, states can develop regulations that are more stringent or broader in scope than the EPA's.

The State of Utah has been authorized by EPA to operate the RCRA program in that state. The DSHW administers the RCRA program, including the LDR program. DSHW adopted EPA's RCRA characteristics and lists of hazardous wastes. Because DPG, DCD, TOCDF, and CAMDS have missions associated with chemical agents, in July 1988 the DSHW modified its

regulations under R315-2-11 to include chemical agents and associated wastes as hazardous wastes within the state. In addition, under R315-2-10, DSHW included residues from demilitarization, treatment, and testing of the chemicals identified in R315-2-11. At that time, no management standards, such as LDR treatment standards, were developed. In February 1995, the DSHW announced a regulatory initiative to re-examine its current hazardous waste listings for chemical agent wastes and to establish LDR treatment standards for these wastes as part of the Utah Chemical Agent Rule (UCAR).

There are two types of LDR treatment standards: technology based and concentration based. When a technology-based standard applies, wastes must be treated by that technology. When a concentration-based standard applies, wastes must be treated to meet concentration limits established for hazardous constituents. The primary advantage of the technology-based standard is that wastes do not have to be analyzed to prove that treatment standards have been met. The primary advantage of the concentration-based standard is that the facility has greater latitude to determine the most appropriate technology to apply to treat the waste, including emerging and innovative technologies.

An innovative approach has been established with respect to these standards for application under the UCAR. Both technology- and concentration-based standards are proposed for the same listed waste streams, and both standards are to be established on the basis of risk. The technology-based standards must be able to meet the concentration-based standards as a condition of their being proposed as an LDR technology. The U.S. Army (Army) would be permitted to choose which standard would be applied to specific listed waste streams. Under this approach, protection of human health and the environment is ensured, while repeated and expensive analyses are avoided. Another advantage is that when emerging and innovative technologies become available, the rule would permit their use as long as the concentration-based standards are met.

The chemical agent waste streams include agents that become wastes (P901-P910), and wastes that result from treatment of agents (K901-K908). This report assesses the effectiveness of chemical neutralization to treat the various chemical agent waste streams to or below the proposed LDR concentration-based treatment standards identified for the chemical agents in the proposed UCAR.

Wastes U901 and U902, DM and BZ, respectively, are not addressed in this background document. Because a concentration-based LDR standard is not available for these compounds, LDR technologies cannot be established at this time.

1.2 PURPOSE AND SCOPE

The purpose of this report is to support the application of chemical neutralization as an LDR technology for agent related waste streams. Included are waste streams generated by the

Army chemical agent operations at DPG, DCD, TOCDF, and CAMDS. The waste streams listed in the proposed UCAR include both the chemical agents that become wastes (P901-P910) and the chemical agent associated wastes (K901-K908).

This document assesses the ability of chemical neutralization to reduce constituents in the various waste streams to or below the expected LDR concentration standards that are to be established in the UCAR. To be considered applicable, a technology must be capable of treating either the waste in question or a waste that is similar in terms of parameters that affect the selection of the treatment method. Parameters that affect treatment performance may include both physical and chemical characteristics, such as pH, bond disassociation energy, thermal conductivity, inorganic and organic composition, and concentration of constituents of concern. To be considered demonstrated, a technology must be employed in operation for the treatment of the waste in question or a similar waste.

For several Utah-listed chemical agent related wastes for which this background document supports designation of chemical neutralization as a specified LDR treatment standard, other technologies are also capable of treating the wastes to meet the concentration-based standards. Additional background documents have been prepared supporting designation of such technologies as additional specified LDR technologies. Also, the Army is examining a number of new technologies that may prove capable of qualifying as specified LDR technologies. For example, several technologies are being evaluated under the Army's Assembled Chemical Weapons Assessment (ACWA) program. The UCAR includes a proposed quick-action mechanism for designating a new technology as a specified technology.

1.3 REPORT ORGANIZATION

The remainder of this report is organized as follows:

- *Section 2: Industry Affected and Waste Characterization* - This section introduces the chemical agent related industry in Utah that uses chemical neutralization as a treatment technology. It provides information concerning the industry affected, including a description of processes and resulting waste streams, chemical agent properties and reactions, and associated chemical neutralization solutions.
- *Section 3: Support for Chemical Neutralization of Chemical Agent Waste Streams as a Land Disposal Restriction Treatment Technology* - This section describes products of chemical neutralization of the agents identified in Section 2 and presents data to be used in determining if these chemical neutralization procedures are "applicable" and can be considered "demonstrated."

- *Section 4: Summary and Conclusions* - This section briefly summarizes chemical neutralization procedures and products and presents conclusions as to whether the data support chemical neutralization procedures as “applicable” and “demonstrated.”
- *Section 5: References* - This section lists complete citations for the references cited in this report.
- *Appendix A* - This appendix contains a chemical structures dictionary.

Throughout the report, tables are presented as closely to their first text reference as possible.

2 INDUSTRY AFFECTED AND WASTE CHARACTERIZATION

The DPG, DCD, CAMDS, and TOCDF neutralize chemical agents and chemical agent related waste in accomplishment of their missions. Section 2.1 identifies DPG, DCD, CAMDS, and TOCDF as constituting the industry affected and briefly describes their mission and processes used. Section 2.2 characterizes the chemical agents and chemical agent related wastes generated, briefly discusses the chemical neutralization process and describes chemical agents and associated neutralization solutions.

2.1 INDUSTRY AFFECTED AND PROCESS DESCRIPTIONS

This section describes processes and chemical agent related waste streams for the affected industry (DPG, DCD, CAMDS, and TOCDF).

2.1.1 Dugway Proving Ground

Dugway Proving Ground (DPG) generates chemical agent related waste during fulfillment of its mission, which includes developing and testing attack deterrent capabilities, developing and testing methods to protect personnel and equipment from chemical agent attacks, and determining the effects of chemical warfare agents and chemical neutralization solutions on military equipment and supplies. The majority of the chemical agent related waste is generated during chemical neutralization of materials involved in chemical agent testing. The remaining chemical agent related wastes that may be generated at DPG are associated with range-recovered munitions, personal protective equipment, and spilled material and waste.

Table 2.1 lists the chemical agent related waste streams that are generated at DPG and includes information pertaining to chemical neutralization.

2.1.2 Deseret Chemical Depot

Deseret Chemical Depot's (DCD's) mission is storage of the chemical weapons stockpile maintained in Utah. DCD has been storing chemical weapons since 1942. The stockpile consists of spray tanks, cartridges, projectiles, rockets, bombs, ton containers, and mines containing nerve agents tabun (GA), sarin (GB), and VX; the blister agent mustard (H/HD, HT); and lewisite (L). The Army is committed to safely storing these weapons until they are eliminated as part of the Army's Chemical Stockpile Disposal Program. DCD stored a total of 13,616 tons of these materials.

TABLE 2.1 DPG Chemical Agent Related Waste Streams and Chemical Neutralization Status

Waste Stream	Treated by Chemical Neutralization?
"P" of "U" listed waste chemical	Yes.
Protective clothing	Potentially. Protective clothing is decontaminated as part of exit procedures and becomes a waste when it is declared unserviceable.
Decontamination/neutralization fluid	Potentially. Analyzed and shipped off-site to permitted treatment, storage, and disposal facility (TSDF).
Liquid laboratory wastes	Potentially. Analyzed and shipped off-site to permitted TSDF.
Laboratory solid wastes	Potentially. Analyzed and shipped off-site to permitted TSDF.
Miscellaneous metal parts	Potentially. Analyzed and shipped off-site to permitted TSDF.
Plastics	Potentially. Analyzed and shipped off-site to permitted TSDF.
Silver fluoride pads	Potentially. Analyzed and shipped off-site to permitted TSDF.
Spent activated carbon	No. Stored pending suitable treatment/disposal arrangement.
Spill cleanup material	Potentially. Neutralization fluids may be used extensively during the cleanup process. Shipped off-site to permitted TSDF.
Soil	No. Shipped off-site to permitted TSDF.
Styrofoam	Potentially. Analyzed and shipped off-site to permitted TSDF.
Trash and debris	No. Shipped off-site to permitted TSDF.
Water/groundwater	No. Permitted on-site storage.

Experienced and trained workers monitor the storage areas. Regular inspections are performed to monitor for leaks and inspect the condition of the weapons and facilities. The majority of the chemical agent related waste is generated from chemical neutralization and cleanup operations as a result of leaking munitions and from spent activated carbon filters.

Table 2.2 lists the chemical agent related waste streams that are generated at the DCD and includes information pertaining to chemical neutralization.

TABLE 2.2 DCD Chemical Agent Related Waste Streams and Chemical Neutralization Status

Waste Stream	Treated by Chemical Neutralization?
Protective clothing	Potentially. Protective clothing is decontaminated as part of the exit procedures and becomes a waste when declared unserviceable.
Munition bodies and miscellaneous metal parts	Yes. Immersed in neutralization fluid when generated, then evaluated for disposition.
Ton containers	No.
Plastics	Potentially. Analyzed and evaluated for disposition.
Spent activated carbon filters and pre-filters	No. Stored as generated pending suitable treatment/disposal arrangements.
Spill cleanup material	Potentially. Neutralization solutions may be used extensively during the cleanup process.
Silver fluoride pads	Potentially. Analyzed and evaluated for disposition.
Trash and debris	Yes. Immersed in neutralization solutions when generated.
Neutralization fluids	Potentially. Analyzed and evaluated for disposition.
Soil	No. Permitted on-site long-term storage.
Water/groundwater	No. Analyzed and evaluated for disposition.

2.1.3 Chemical Agent Munitions Disposal System

The Chemical Agent Munitions Disposal System (CAMDS) has been in operation since 1979 conducting research, development, and demonstration of various methods of demilitarizing chemical munitions and treating the wastes resulting from demilitarization processes. The chemical agents investigated by CAMDS are the nerve agents GA, GB, and VX, the blister agents H/HD, HT, and L. The current mission is to provide continuing process development and demonstration of integrated munitions demilitarization and waste treatment plants and processes.

CAMDS operates as a treatment, storage, and disposal facility (TSDF) to demonstrate and refine baseline and alternative technologies. The general activities are munitions handling and disassembly; incineration of wastes resulting from munitions handling; pollution abatement systems associated with incineration and munitions handling; and treatment of wastes such as scrap metal, brines, and ash to minimize the amount of waste requiring disposal. Information generated aids in the technical and economic feasibility evaluation of munitions handling

equipment, incinerators, pollution abatement systems, and alternative treatment methods. CAMDS waste treatment units consist of fabricated equipment reflecting state-of-the-art technology.

The units at CAMDS are sized to handle actual munitions at rates that demonstrate the processes involved. The equipment and process control technologies provide reliability data for demilitarization of chemical munitions, extended operations maintenance evaluation, incineration of actual munitions components and chemical agents, control of integrated processes, and treatment of flue gases and solid residues.

DCD's entire stockpile of lewisite, 10 ton containers, will be destroyed at CAMDS through a chemical neutralization process originally developed in 1991 by Chem-Security Ltd. to destroy the Canadian stockpile of lewisite. Lewisite is converted to sodium arsenate in a three-step batch process. CAMDS has already received a RCRA research, development, and demonstration (RD&D) permit and an air quality permit for this process, with operation scheduled to begin in early 1999.

Table 2.3 lists the chemical agent related waste streams that are generated at the CAMDS and includes information pertaining to chemical neutralization.

2.1.4 Tooele Chemical Destruction Facility

The chemical agent stockpile stored at the DCD is scheduled for processing at the Tooele Chemical Destruction Facility (TOCDF). It consists of various projectiles, ton containers, rockets, bombs, mines, and spray tanks. The bulk of the chemical agent stockpile stored at DCD contains GB, HD, and VX, with smaller amounts of H/HD, HT, GA, and lewisite. The lewisite is not scheduled for processing at TOCDF; it will be processed at CAMDS. The TOCDF treatment process is based on disassembly of munitions followed by separation and destruction of individual components by incineration. The initial processing step involves disassembly with the removal of explosives and draining of the chemical agent from projectiles or the draining of chemical agent from ton containers. Rockets and mines are sheared into sections and punched, respectively. Agent is drained from the rockets and mines during the shearing and punching operations. The drained agents are incinerated in the liquid incinerator (LIC). The deactivation furnace system (DFS) processes drained rockets and mines and the energetic components of the munitions. The metal parts furnace (MPF) thermally decontaminates all drained ton containers and drained munitions other than rockets and mines. Liquid agent related waste streams are processed in the LIC, and the solid agent related waste streams are processed in the MPF.

Table 2.4 lists the chemical agent related waste streams that are generated at the TOCDF and includes information pertaining to chemical neutralization.

TABLE 2.3 CAMDS Chemical Agent Related Waste Streams and Chemical Neutralization Status

Waste Stream	Treated by Chemical Neutralization?
"P" listed waste chemicals	Potentially.
Brine reduction area baghouse residue	No.
Brine salts	No.
Decontamination/neutralization fluid	Potentially. If agent concentration is greater than 20 ppb for GA, GB, and VX; 200 ppb for H/HD/HT; and 1 ppm for L.
Deactivation furnace system (DFS) cyclone residue	No.
DFS ash	No.
DFS refractory	No.
Demilitarization protective ensemble (DPE) suits	No. DPE suited personnel are decontaminated as part of the exit procedure. DPE suits are not considered a waste until after they are removed.
Liquid laboratory wastes	Potentially. If agent concentration is greater than 20 ppb for GA, GB, and VX; 200 ppb for H/HD/HT; and 1 ppm for L.
Laboratory solid wastes	Yes.
Miscellaneous metal parts	Potentially. Metal parts are either surface decontaminated or processed through the metal parts furnace (MPF).
Mist eliminator filters/demister candles	No. Not agent contaminated.
Metal parts furnace ash	No.
Metal parts furnace metal	No.
Metal parts furnace refractory	No.
Pollution abatement system brine	No.
Pollution abatement system brine sump sludge	No.
Plastics	No. Typically containerized, headspace monitored, then placed in storage. No permitted treatment method established yet.
Soil	No. Shipped to treatment, storage, and disposal facility (TSDF).
Spent activated carbon	No. Stored as generated pending suitable treatment/disposal arrangement.
Spent hydraulic fluid	No.
Spent silver fluoride pads	Potentially.
Spill cleanup material	Potentially. Neutralization fluids may be used extensively during the cleanup process.
Styrofoam	Potentially.
Trash and debris	Potentially. Stored as generated until suitable treatment method is established.
Waste oil	Potentially. Shipped to TSDF.
Wooden pallets	Potentially. Shipped to TSDF.
Lewisite	Yes.

TABLE 2.4 TOCDF Chemical Agent Related Waste Streams and Chemical Neutralization Status

Waste Stream	Treated by Chemical Neutralization?
"P" listed waste chemicals	No.
Brine reduction area baghouse residue	No.
Brine salts	No.
Brine tank sludge	No.
Decontamination/neutralization fluid	Potentially. If agent concentration is greater than 20 ppb for GB and VX and 200 ppb for H/HD/HT.
Deactivation furnace system (DFS) cylinder residue	No.
DFS Heated Discharge Conveyor ash	No.
DFS refractory	No.
Demilitarization protective ensemble (DPE) suits	No. DPE suited personnel are decontaminated as part of the exit procedure. DPE suits are not considered waste until after they are removed.
Laboratory liquid waste	Potentially. If agent concentration is greater than 20 ppb for GB/VX or 200 ppb for H/HD/HT.
Laboratory solid waste	Yes. Agent associated laboratory waste is treated in satellite accumulation container by immersion in bleach.
Liquid incinerator ash/slag	No.
Liquid incinerator refractory	No.
Miscellaneous metal parts	Potentially. Metal parts are either surface decontaminated or processed through the metal parts furnace (MPF).
Mist eliminator filters/demister candle	No. Not agent contaminated.
MPF ash	No.
MPF metal	No.
MPF refractory	No.
MPF residue	No.
Pollution abatement system (PAS) brine	Normally not agent contaminated. If agent concentration is above 20 ppb GB/VX or 200 ppb H/HD/HT, neutralization solution is added to the brine.
PAS brine sump sludge	No. Not agent contaminated.
PAS quench tower residue	No.
Plastics	No. Typically containerized, headspace monitored, then placed in storage.
Residue handling area (RHA) baghouse residue	No.

TABLE 2.4 (Cont.)

Waste Stream	Treated by Chemical Neutralization?
Spent activated carbon	No. Stored as generated until suitable treatment method is established.
Spent hydraulic fluid	No.
Silver fluoride pads	Potentially.
Spill cleanup material	Potentially. Neutralization solution may be used extensively during the cleanup process.
Trash and debris	Potentially. Stored as generated until suitable treatment method is established.
Waste oil	Potentially.
Wooden pallets	Potentially. Permitted on-site storage.

2.2 CHEMICAL AGENT CHARACTERIZATION AND CHEMICAL NEUTRALIZATION SOLUTIONS

Chemical agents stored, tested, and destroyed in the Army's facilities in Utah fall into two basic categories: nerve agents and blister (vesicant) agents. Both categories contain several chemical agents. Several chemical neutralization solutions of various strengths are routinely used for neutralization of these chemical agents and chemical agent related wastes. The treatments can be separated into two categories on the basis of the type of chemical neutralization reaction. One category of chemical neutralization reactions is oxidation. The hypochlorite bleaches neutralize by oxidation. The other important chemical neutralization reaction is alkaline hydrolysis, which proceeds by the reaction of hydroxide ion with the chemical agents. Alkaline hydrolysis reaction pathways and rates depend upon pH, temperature, and solvent. At an alkaline pH, hypochlorite solutions act universally against the nerve agents and vesicants by providing both oxidation and alkaline hydrolysis (US Army Medical Research Institute of Chemical Defense 1995). Table 2.5 presents the specific agents managed at each of the Army's facilities in Utah. A detailed description of each agent is presented in Section 2.2.1. Tables 2.6 through 2.9 list the neutralization solutions used at each facility. These solutions are discussed in more detail in Section 2.2.2.

2.2.1 Properties and Reactions of Chemical Agents under Neutralization Conditions

This section describes the properties and reactions of the chemical agents. After presentation of some general information about chemical agent properties and reactions, additional information on nerve agents and blister agents is presented. For each chemical agent,

TABLE 2.5 Chemical Agents by Location

Chemical Agent Category	Chemical Agent Acronym	Location Stored, Tested, and/or Neutralized ^a			
		DPG	DCD	CAMDS	TOCDF
Nerve agents	GA	X	X	X	X
	GB	X	X	X	X
	GD	X			
	TGD	X			
	GF	X			
	VX	X	X	X	X
	Vx	X			
Blister agents	H/HD	X	X	X	X
	HL	X			
	HT	X	X	X	X
	HQ	X			
	L	X	X	X	
	HN1	X			
	HN3	X			

^a An "X" indicates that the chemical agent may be stored, tested, and potentially chemically neutralized at that facility.

TABLE 2.6 Chemical Neutralization Solutions Used at DPG

Neutralization Solution Category	Neutralization Solution	Neutralization Solution Acronym and Comments
Chlorinated bleaches (oxidation reactions)	A minimum of 5% aqueous sodium hypochlorite	NaOCl in water
	10% aqueous supertropical bleach (supertropical bleach [STB] slurry)	STB is calcium chlorohypochlorite [CaCl(OCl)] with some calcium oxide (CaO)
	10% aqueous high-test hypochlorite (high-test hypochlorite [HTH] slurry)	HTH is calcium hypochlorite [Ca(OCl) ₂]. HTH contains twice the available chlorine found in STB
Caustics (alkaline hydrolysis reactions)	Caustic alcohol solution (10% NaOH in alcohol)	A minimum of 10% sodium hydroxide (NaOH) in an 80/20 mixture of denatured ethanol (EtOH) and water
	A minimum of 10% aqueous sodium hydroxide	NaOH in water
	A minimum of 10% aqueous sodium carbonate	Na ₂ CO ₃ in water
	Concentrated ammonia	NH ₄ OH

TABLE 2.7 Chemical Neutralization Solutions Used at DCD

Neutralization Solution Category	Neutralization Solution	Neutralization Solution Acronym and Comments
Chlorinated bleach (oxidation reactions)	10% aqueous calcium hypochlorite (HTH)	Calcium hypochlorite (HTH is calcium hypochlorite [Ca(OCl) ₂])
	50 lb STB to 6 gal water	STB Slurry (STB is calcium chlorohypochlorite)
	Commercial bleach, full strength	Bleach (sodium hypochlorite)
Caustics (alkaline hydrolysis reactions)	10% aqueous sodium hydroxide	Sodium hydroxide (NaOH in water)
	10% aqueous sodium carbonate	Sodium carbonate (Na ₂ CO ₃ in water)

TABLE 2.8 Chemical Neutralization Solutions Used at CAMDS

Neutralization Solution Category	Neutralization Solution	Neutralization Solution Acronym and Comments
Chlorinated bleach (oxidation reactions)	7% aqueous sodium hypochlorite	Sodium hypochlorite (NaOCl in water)
Caustics (alkaline hydrolysis reactions)	18% aqueous sodium hydroxide	Sodium hydroxide (NaOH in water)
	8-10% aqueous sodium carbonate	Sodium carbonate (Na ₂ CO ₃ in water)

TABLE 2.9 Chemical Neutralization Solutions Used at TOCDF

Neutralization Solution Category	Neutralization Solution	Neutralization Solution Acronym and Comments
Chlorinated bleach (oxidation reactions)	12% aqueous sodium hypochlorite	Sodium hypochlorite (NaOCl in water)
Caustics (alkaline hydrolysis reactions)	18% aqueous sodium hydroxide	Sodium hydroxide (NaOH in water)

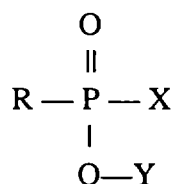
the Chemical Abstracts Service Registry Number (CAS Reg. No.) and synonyms are listed. More than one CAS Reg. No. is listed for some of the chemical agents because they exist as isomers. In such situations, the first CAS Reg. No. applies to the commonly produced mixture of isomers of that agent. The additional CAS Reg. Nos. apply to individual isomers and to other mixtures. Structures for each chemical agent are presented in Appendix A. The chemical reactions pertinent to chemical neutralization are discussed, and tables of environmentally relevant properties are included.

The chemical agents are reactive molecules by design. They are capable of a variety of chemical reactions under different conditions that may result in different products of reaction. Key reaction conditions for a particular agent may include pH, relative ratios of neutralization solution to agent, the solvent system, the amount of stirring, and/or temperature. The following example demonstrates the effect of the solvent system on the products of reaction. The reaction of VX with hydroxide ion in water yields several products, one of them being a compound called S-(2-diisopropylaminoethyl) methylphosphonothioic acid (EA2192). EA2192 is formed from VX at medium and high pH values. EA2192 does not break down readily by further reaction with hydroxide ion. However, experiments with a VX simulant indicate that the same materials (VX + hydroxide ion) reacted in a solution of 90% ethanol (EtOH) would not produce EA2192 because in EtOH the reaction favors a different reaction pathway.

The reaction of distilled levinstein mustard (HD) with hydroxide ion is an example of the effect of stirring on the products of reaction. When a large volume of HD was added to 2.5 times its volume of concentrated sodium hydroxide solution and left unstirred for a month, at least 25 compounds formed and some of the HD was left unchanged. However, when HD is stirred with a 20-fold volume of sodium hydroxide solution, it reacts to form thiodiglycol. Chemical neutralization practices therefore include adding excess sodium hydroxide solution and stirring.

2.2.1.1 General Chemistry of the Nerve Agents

The nerve agents have similar properties because they all contain a phosphorus atom with four substituents around it. The differences among the nerve agents result from the presence of different substituents around the central phosphorus atom. The tetracoordinated phosphorus atom may be represented generally as follows:



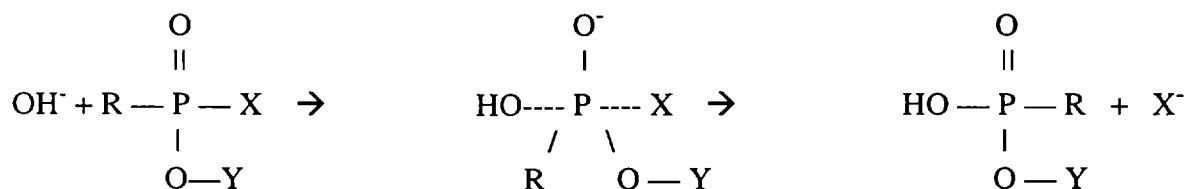
where O is oxygen. The other substituents are given in Table 2.10.

TABLE 2.10 Nerve Agent Substituents^a

Chemical Agent	R	Y	X
GA	Dimethylamino group – N(CH ₃) ₂	Ethyl group – CH ₂ CH ₃	Cyano group (CN)
GB	Methyl group – CH ₃	Isopropyl group – CH(CH ₃) ₂	Fluorine (F)
GD	Methyl group – CH ₃	Pinacolyl group – CH(CH ₃)C(CH ₃) ₃	Fluorine (F)
GF	Methyl group – CH ₃	Cyclohexyl group – C ₆ H ₁₁	Fluorine (F)
VX	Methyl group – CH ₃	Ethyl group – CH ₂ CH ₃	N,N-diisopropylmercaptoethyl group – SCH ₂ CH ₂ N(iC ₃ H ₇) ₂
Vx	Methyl group – CH ₃	Iso-butyl group – CH ₂ CH(CH ₃) ₂	N,N-diethyl mercaptoethyl group – SCH ₂ CH ₂ N(C ₂ H ₅) ₂

^a “R”, “Y”, and “X” refer to the substituent positions in the tetracoordinated structure on the previous page.

One of the important reactions of the nerve agents is a second-order nucleophilic substitution (S_N2) reaction (also called an addition-elimination reaction) at the tetracoordinate phosphorus (Jody et al. 1983). The nucleophile, an ion with a stronger affinity for the phosphorus atom than one of the other bonded groups, displaces the group with the weakest affinity. In the case of alkaline hydrolysis, the hydroxide ion acts as a nucleophile to displace the “X” groups in Table 2.10. The S_N2 reaction proceeds through a pentacoordinate intermediate:



In the case of phosphonate esters, of which the nerve agents are an example, the rates of hydroxide ion (OH[–]) displacement of the leaving group can be correlated fairly closely with the pK_a of the displaced anion (Epstein et al. 1974, cited in Jody et al. 1983). The correlation of hydrolysis reaction rate with pK_a holds up well for the G-agents. It does not apply as well to VX with its multiple reaction pathways (Yang et al. 1992). S_N2 hydrolysis is the principal chemical neutralization reaction for the G agents, and it is one of the reaction pathways open to VX.

In their discussion of the kinetics of alkaline hydrolysis of the nerve agents, Durst et al. (1988) noted that the rate of hydrolysis in aqueous base will have contributions from water and from hydroxide reacting with the agent. Because the hydrolysis is an S_N2 reaction, the rate equation will take a second-order form:

$$\text{rate} = k_1[\text{H}_2\text{O}][\text{agent}] + k_2[\text{OH}^-][\text{agent}] .$$

Because water is present in large excess and its concentration is not significantly changed by the reaction with agent, the concentration of water behaves like a constant in the rate equation. That allows the equation to be rewritten as:

$$\text{rate} = k_{\text{water}}[\text{agent}] + k_{\text{OH}}[\text{OH}^-][\text{agent}]$$

and factored to become:

$$\text{rate} = (k_{\text{H}_2\text{O}} + k_{\text{OH}}[\text{OH}^-]) [\text{agent}] .$$

Experimental studies have shown $k_{\text{H}_2\text{O}}$ to be a very small term compared to $k_{\text{OH}}[\text{OH}^-]$ under the high pH conditions of alkaline hydrolysis. In view of that, the equation can be simplified to the form commonly used to describe the rate of alkaline hydrolysis of the nerve agents:

$$\text{rate} = k_{\text{OH}}[\text{OH}^-][\text{agent}] .$$

Alkaline hydrolysis of the nerve agents commonly is carried out at high pH with an excess of chemical neutralization solution. Thus, for a particular chemical neutralization process, the $[\text{OH}^-]$ is present in large excess and its concentration is not significantly changed by reaction with the agent. This situation allows the equation for neutralization at a particular pH to be further simplified by treating $k_{\text{OH}}[\text{OH}^-]$ as a constant for that pH. Setting $k_{\text{OH}}[\text{OH}^-] = k_{\text{obs}}$, the equation becomes “pseudo first-order”:

$$\text{rate} = k_{\text{obs}} [\text{agent}] .$$

One advantage of a first-order reaction is that its half-life, which is the time for one-half of the starting material to disappear, is independent of concentration and can be calculated from the following equation:

$$t_{1/2} = (\ln 2)/k_{\text{obs}} = 0.693/k_{\text{obs}} .$$

With experimentally determined k_{OH} values for the different nerve agents, the rate of chemical neutralization by alkaline hydrolysis can be predicted for those agents at different pH

levels. In practice, the rate constants sometimes include a temperature correction term to allow prediction of neutralization rates at different temperatures.

Table 2.11 lists the experimentally determined values for k_{OH} for four nerve agents, along with the corresponding half-lives at pH = 12 (Durst et al. 1988). Table 2.11 indicates that it would take 3 seconds to reduce the concentration of GB from 1 mole/liter to 0.5 mole/liter. It also would take 3 seconds to reduce the concentration of GB from 0.01 mole/liter to 0.005 mole/liter.

In general, the time required for chemical neutralization of an agent by alkaline hydrolysis to a specific level can be estimated with the half-life of the neutralization reaction. A value for the half-life is obtained by using the assumptions reviewed in the preceding paragraphs:

- The contribution of water to the hydrolysis process is assumed to be very small in comparison with the contribution of the hydroxide ion.
- The hydroxide ion is assumed to be present in such excess that its concentration is not reduced significantly by the chemical neutralization process.

The following example is of an “agent” with a molecular weight of 100 and an adequate excess of hydroxide ion. Starting with an initial quantity of 100 grams of chemical agent, 50 grams would be left after one half-life had elapsed. At the end of the second half-life, 25 grams would remain. The quantity remaining after “n” half-lives is given by the relationship:

$$\text{Quantity Remaining} = (\text{Initial Quantity})/2^n = 100/2^n.$$

Table 2.12 tracks the amount of “agent” remaining through ten half-lives, values for 15 and 20 half-lives are given as well (Durst et al. 1988). The data show that exposure to neutralization solution for 10 half-lives achieves greater than 99.9% destruction of agent, while exposure for 20 half-lives achieves greater than 99.999% destruction.

TABLE 2.11 Half-Lives of Nerve Agents

Chemical Agent	k_{OH} ($M^{-1} s^{-1}$)	$t_{1/2}$ (s) at pH = 12
GA	7.5	9.2
GB	25	3
GD	10	7
VX	0.083	835

TABLE 2.12 Quantity of Chemical Agent Remaining after the Specified Number of Half-Lives

Initial Quantity (grams)	Half-Lives	Quantity Remaining (grams)	% Destroyed
100	0	100	0
100	1	50	50
50	2	25	75
25	3	12.5	87.5
12.5	4	6.25	93.75
6.25	5	3.125	96.875
3.125	6	1.5625	98.4375
1.5625	7	0.78125	99.21875
0.78125	8	0.390625	99.609375
0.390625	9	0.1953125	99.804687
0.1953125	10	0.0976562	99.902343
0.0061035	15	0.0030517	99.996946
0.0001907	20	0.0000953	99.999899

2.2.1.2 General Chemistry of the Blister Agents

The blister agents (vesicants) fall into three categories: the sulfur mustards (H/HD, HT, and HQ), the nitrogen mustards (HN1 and HN3), and lewisite. They have similar properties because they are lipid soluble and because of the structural relationship between the chlorine atom(s) and the neighboring hetero-atom: sulfur, nitrogen, or arsenic. In H/HD, the chlorine atoms are separated from the hetero-atom by two carbon atoms. However, the relationship between structure and vesicancy is not simple. For example, mustard with the formula $(\text{ClCH}_2\text{CH}_2)_2\text{S}$ is a potent blister agent, while the disulfide, $(\text{ClCH}_2\text{CH}_2)_2\text{S}_2$, and higher polysulfides, $(\text{ClCH}_2\text{CH}_2)_2\text{S}_x$, are much less potent.

The chemical neutralization of blister agents also is complicated. The hydrolysis of HD is highly dependent on the reaction conditions. Under ideal conditions (a large excess of water, high pH, and adequate stirring) HD can be hydrolyzed almost exclusively to thiodiglycol and chloride ion. Departure from those conditions can result in a variety of reaction products (Rosenblatt et al. 1995). For that reason, hydrolysis is not recommended for the chemical neutralization of the sulfur mustards. Therefore, hypochlorite oxidation is the chemical neutralization process commonly used for that group. Yurow and Davis (1982) have stated that the stoichiometry of the hypochlorite oxidation of HD is indefinite because of the many products formed. An excess of hypochlorite is necessary for complete reaction. Significant heat is produced during the reaction (Yurow and Davis 1982). Samuel and co-workers (1998) recently found that a mole ratio of 1:5 to 1:14 for HD:hypochlorite is necessary to complete the chemical neutralization process. The outcome also depends upon the pH.

The pH also plays an important role in determining the products from the hydrolysis of the nitrogen mustards (Yurow and Davis 1982) and of lewisite (Durst et al. 1988). The nitrogen

mustards and lewisite can be neutralized successfully by alkaline hydrolysis at a sufficiently high pH.

In summary, the physiological action and chemical neutralization of the blister agents do not fit a straightforward pattern. The sulfur mustards (H/HD, HT, and HQ) have some common characteristics, as do the nitrogen mustards (HN1 and HN3). Otherwise, it is necessary to consider the blister agents individually.

2.2.1.3 GB (Sarin)

CAS Reg. No.: 107-44-8 (also 50642-23-4, 6171-93-3, 6171-94-4)

Synonyms:

Methyl-isopropyl ester phosphonofluoridic acid
 Methyl-1-methylethyl ester phosphonofluoridic acid
 Isopropyl methylphosphonofluoridate
 Isopropyl ester of methylphosphonofluoridic acid
 Methylisopropoxyfluorophosphine oxide
 Isopropyl methylfluorophosphonate
 O-Isopropyl methylphosphonofluoridate
 Isopropyl ester methylfluorophosphonic acid
 Isopropoxymethylphosphonyl fluoride
 Zarin
 EA1208

Properties: GB is fairly volatile, and, therefore, is a relatively nonpersistent nerve agent. It evaporates at about the same rate as water (Field Manual 3-9 [Departments of the Army, Navy, and Air Force 1990]). Table 2.13 summarizes additional environmentally relevant data concerning GB (Rosenblatt et al. 1995).

Reactions: GB is infinitely soluble in water and will hydrolyze under acidic, neutral, and basic conditions. The rate of hydrolysis is slowest in the pH range 4 to 6. GB has a hydrolytic half-life of about 160 hours at pH 5 and 25°C. The rate of hydrolysis increases below pH 4 and above pH 6, increasing rapidly with increasing hydroxide ion concentration. When large amounts of GB are added to distilled water, the observed hydrolysis rate first decreases but then increases once the pH has dropped through the minimum reaction rate range and acid catalysis begins to

TABLE 2.13 Environmentally Relevant Properties of GB

Property	Data	Data Quality	Reference
Empirical formula	C ₄ H ₁₀ FO ₂ P	Not applicable	
Molecular weight	140.1 g/mol	Not applicable	
Liquid density	1.0887 g/mL at 25°C	Good	Samuel et al. 1983, cited in Rosenblatt et al. 1995
Melting point	-56.9°C	Fair	Samuel et al. 1983, cited in Rosenblatt et al. 1995
Boiling point	157.8°C	Good	Samuel et al. 1983, cited in Rosenblatt et al. 1995
Heat of vaporization	80.66 cal/g	Good	Samuel et al. 1983, cited in Rosenblatt et al. 1995
Vapor pressure (torr)	2.94/25°C	Good	Samuel et al. 1983, cited in Rosenblatt et al. 1995
Log K _{OW}	0.15 (2)	Poor	Britton and Grant 1988, cited in Rosenblatt et al. 1995
	0.299	Not available	U.S. Army 1999
Aqueous solubility (g/L)	Miscible in all proportions.	Good	Field Manual 3-9 ^a
K _H (atm·m ³ /mol)	4.0 × 10 ⁻⁷ /25°C	Poor	Preston and Starrock 1993, cited in Rosenblatt et al. 1995
Diffusion coefficient (air)	0.061 cm ² /s at 25°C	Fair	Samuel et al. 1983, cited in Rosenblatt et al. 1995
	0.1 cm ² /s at 300 K	Not available	U.S. Army 1999
Log K _{OC}	0.45	Poor	Rosenblatt et al. 1995
	1.8	Not available	Small 1984, cited in Rosenblatt et al. 1995
	1.54	Not available	U.S. Army 1999

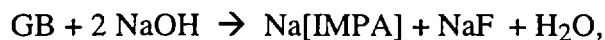
^a Departments of the Army, Navy, and Air Force (1990).

take effect (Clark 1989, cited in Rosenblatt et al. 1995). The second-order rate constant for the hydroxyl-ion catalyzed hydrolysis of GB is:

$$\log k_2 (\text{M}^{-1} \text{min}^{-1}) = 9.8507 - (1,985.4/T_K).$$

At 25 °C and at pH 10, the half life of GB is 5 minutes (Demek et al. 1970, cited by Rosenblatt et al. 1995).

The alkaline hydrolysis products of GB are fluoride ion and the sodium salt of isopropyl methylphosphonic acid (IMPA):



where Na[IMPA] is the sodium salt of IMPA.

The heat of reaction (enthalpy) is -44.4 kilocalories per mole (kcal/mol) (Davis et al. 1979). Thermodynamic calculations predict substantially complete conversion of GB to IMPA. The calculated equilibrium constant is $\log K_{\text{eq}} = 21.9$ based upon a free energy of -30,000 cal/mol. Nuclear magnetic resonance (NMR) spectroscopy data confirm that IMPA is the sole phosphorus-containing product of the alkaline hydrolysis of GB down to 0.5% (Durst et al. 1988).

When GB is chemically neutralized with 5.25% NaOCl in water, the reaction is an alkaline hydrolysis, and the products are the sodium salt of IMPA and fluoride ion (Durst et al. 1988). The second-order rate constant for this reaction is larger ($10 \text{ M}^{-1} \text{ s}^{-1}$ at 25°C) than that for hydrolysis with OH^- . This condition is attributed to the catalytic effect of hypochlorite (OCl^-) upon the reaction. When large amounts of GB are neutralized with hypochlorite, additional hydroxide must be added to the hypochlorite solution to maintain the pH (Yurow and Davis 1982).

Because of the sensitivity of GB to hydrolysis, there has been a problem with it decomposing in munitions. N,N'-diisopropylcarbodiimide and/or tributylamine have been added as stabilizers. Up to 0.5% of the starting material, methylphosphonic difluoride, and some diisopropylmethylphosphonate (DIMP), an impurity, may also be present in weapons-grade GB. The N,N'-diisopropylcarbodiimide hydrolyzes to N,N'-diisopropyl urea (Rosenblatt et al. 1995). Tributylamine is unaffected by aqueous hydrolysis. Methylphosphonic difluoride hydrolyzes rapidly at high pH to form the ions of methylphosphonic acid (MPA) and fluoride. The dialkyl ester, DIMP, undergoes slow hydrolysis at high pH to form the monoalkyl ester, isopropylmethylphosphonic acid. Similar stabilizers and impurities may be associated with the other G agents (Rosenblatt et al. 1995).

2.2.1.4 GA (Tabun)

CAS Reg. No.: 77-81-6 (also 93957-08-5, 93957-09-6)

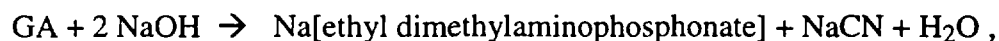
Synonyms:

Ethyl N,N-dimethylphosphoramidocyanidate
 Ethyl dimethylphosphoramidocyanidate
 Dimethylaminoethoxy-cyanophosphine oxide
 Dimethylamidoethoxyphosphoryl cyanide
 Ethyl dimethylaminocyanophosphonate
 Ethyl ester of dimethylphosphoroamidocyanidic acid

Ethyl phosphorodimethylamidocyanidate
EA1205

Properties: Table 2.14 lists the environmentally relevant properties of GB. The data quality of these properties has not been evaluated.

Reactions: The reaction of GA is similar to that of GB, GD, and GF. GA is reacted with an excess of OH⁻ in water to produce the anion of ethyl dimethylaminophosphonic acid and cyanide ion. The equation for the reaction of GA with NaOH is:



where Na[ethyl dimethylaminophosphonate] is the sodium salt of ethyl dimethylaminophosphonic acid and NaCN is sodium cyanide.

TABLE 2.14 Environmentally Relevant Properties of GA

Property	Data	Reference
Empirical formula	C ₅ H ₁₁ N ₂ O ₂ P	Field Manual 3-9 ^a
Molecular weight	162.13 g/mol	Field Manual 3-9
Liquid density	1.073 g/mL at 25°C	Field Manual 3-9
Melting point	-50°C	Field Manual 3-9
Boiling point	240°C 220°C to 246°C/760 mm Hg	Material Safety Data Sheet for GA Field Manual 3-9
Heat of vaporization	79.56 cal/g	Field Manual 3-9
Vapor pressure	0.037 mm Hg at 20°C	Field Manual 3-9
Log K _{OW}	0.07 mm Hg at 25°C 0.384	Edgewood Arsenal 1974 U.S. Army 1999
Aqueous solubility	9.8% at 25°C 7.2% at 20°C	Field Manual 3-9
K _H (atm·m ³ /mol)	Not available	Not available
Diffusion coefficient (air) (cm ² /s)	0.092 at 300 K	U.S. Army 1999
Log K _{OC}	1.59	U.S. Army 1999
Volatility	858 mg/m ³ at 30°C 610 mg/m ³ at 25°C 328 mg/m ³ at 20°C 90 mg/m ³ at 0°C	Field Manual 3-9

^a Departments of the Army, Navy, and Air Force (1990).

The pseudo first-order rate constant for the hydrolysis of GA by hydroxide ion has been reported as 0.02 min^{-1} at pH 9.5 and 25°C . The associated heat of reaction has been reported as -10.1 kcal/mole . Under acidic conditions, the hydrolysis of GA produces dimethylamine (Yurow 1988). NMR has confirmed the disappearance of GA and the appearance of the anion of ethyl dimethylaminophosphonic acid (Durst et al. 1988). When sufficient quantities of GA are chemically neutralized with aqueous hydroxide, it becomes necessary to destroy the cyanide ion that is produced to prevent formation of hydrogen cyanide (HCN) if the solution is acidified. After neutralization is complete, treating the solution with hypochlorite converts the cyanide to nitrogen gas and carbonate ion (Yurow and Davis 1988):



Alternatively, GA can be chemically neutralized using a solution of hypochlorite. Both the cyano group and the dimethylamino group are lost, producing the ethyl ester of phosphonic acid. Durst et al. (1988) did not identify the other products of the reaction. Dimethyl amine may be a product.

2.2.1.5 GD (Soman)

CAS Reg. No.: 96-64-0 (also 22956-47-4, 22956-48-5)

Synonyms:

Pinacolyl methylphosphonofluoridate
EA1210

Properties: GD has a solubility of 2.1% in water at 20°C , making it significantly less soluble than GB. GD is a less volatile, and therefore a more persistent agent, than GB. It evaporates at about one-fourth the rate of water (Field Manual 3-9). Table 2.15 presents additional environmentally relevant data concerning GD.

Reactions: The hydrolytic half-life of GD is longest in the pH range of 4 to 7, about 144 hours at pH 5 and 20°C . The rate of hydrolysis increases in more alkaline or more acidic solutions. When large amounts of GD are added to distilled water, the observed hydrolysis rate first decreases, but then increases once the pH has dropped through the minimum reaction rate range and acid catalysis begins to take effect (Clark 1989, cited in Rosenblatt et al. 1995). Healy (1948, cited in Rosenblatt et. al. 1995) reports that the observed hydrolysis rate constant at 25°C , exclusive of buffer effects, is:

$$k_{\text{obs}} (\text{h}^{-1}) = 0.0047 + 33 [\text{H}_3\text{O}^+] + 5 \times 10^4 [\text{OH}^-] .$$

TABLE 2.15 Environmentally Relevant Properties of GD

Property	Data	Data Quality	Reference
Empirical formula	C ₇ H ₁₆ FO ₂ P	Not applicable	
Molecular weight	182.18 g/mol	Not applicable	
Liquid density	1.0223 g/mL at 25°C	Good	Samuel et al. 1983, cited in Rosenblatt et al. 1995
Melting point	-42°C	Fair	Samuel et al. 1983, cited in Rosenblatt et al. 1995
Boiling point	197.8°C	Good	Samuel et al. 1983, cited in Rosenblatt et al. 1995
Heat of vaporization	72.5 cal/g	Good	Samuel et al. 1983, cited in Rosenblatt et al. 1995
Vapor pressure (torr)	0.40/25°C	Good	Samuel et al. 1983, cited in Rosenblatt et al. 1995
	0.274/20°C	Good	Material Safety Data Sheet for GD
Log K _{OW}	1.02	Poor	Britton and Grant 1988, cited in Rosenblatt et al. 1995
	1.79	Not available	Rosenblatt et al. 1995
	1.60	Not available	Rosenblatt et al. 1995
	1.82	Not available	U.S. Army 1999
Aqueous solubility	34 g/L at 0°C	Fair	Edgewood Arsenal 1974, cited in Rosenblatt et al. 1995
	21 g/L at 20°C	Fair	Samuel et al. 1983, cited in Rosenblatt et al. 1995
K _H (atm·m ³ /mol)	3.1 x 10 ⁻⁶ /20°C	Poor	Rosenblatt et al. 1995
Diffusion coefficient (air)	0.047 cm ² /s at 25°C	Fair	Samuel et al. 1983, cited in Rosenblatt et al. 1995
	0.082 cm ² /s at 300 K	Not available	U.S. Army 1999
Log K _{OC}	1.17	Poor	Rosenblatt et al. 1995
	2.37	Not available	U.S. Army 1999

The half-life of GD in excess 5% aqueous sodium hydroxide is 0.08 hour at 20°C. The heat of reaction is estimated to be similar to that of GB (-44.4 kcal/mole) because fluorine is the leaving group in both cases (Yurow 1988). The alkaline hydrolysis of GD produces the anion of pinacolyl methylphosphonic acid (PMPA) and fluoride ion. NMR data confirm that the anion of PMPA is the sole phosphorus-containing product of the alkaline hydrolysis of GD down to 0.5% (Durst et al. 1988):



where Na[PMPA] is the sodium salt of PMPA.

Because GD is comparatively insoluble in water, the use of a solvent mixture consisting of a small proportion of water and a large proportion of methanol (or another alcohol) can increase the solubility and, therefore, the effective rate of neutralization. The alcohol in solution does not significantly inhibit the reactivity of GD, or the other G agents, with hydroxide ion. The solution of hydroxide in methanol forms methoxide ion. The methoxide ion also reacts as a nucleophile to attack the central phosphorus atom to form the ester, methyl pinacolyl methylphosphonate. This ester eventually undergoes hydrolysis to form PMPA and perhaps some methyl methylphosphonic acid (Rosenblatt et al. 1995).

When GD is chemically neutralized with 5.25% NaOCl in water, the reaction is an alkaline hydrolysis, and the products are the anion of pinacolyl methylphosphonic acid and fluoride ion (Durst et al. 1988). Although the rate constant for this reaction has not been determined, it is expected to be similar to that for the analogous GB reaction (Rosenblatt et al. 1995).

2.2.1.6 TGD (Thickened Soman)

CAS Reg. No.: Not Available.

Synonyms: None.

Properties: TGD is GD thickened with a polymer. The compound UCON 75-H-90,000 is a polyethylene glycol derivative that has been used to thicken GB, a related G-agent. Thickeners are added to GD to increase persistence in the field. In general, thickened agents form large droplets that result in a greater concentration reaching the ground and a greater contact hazard than the unthickened forms (Field Manual 3-9). The environmentally relevant properties of TGD are the same as those of GD.

Reactions: Yang and coworkers (1992) have noted that an organic solvent often is added to an aqueous neutralization solution to improve solubility of thickened agents. The neutralization reaction remains the same for the thickened agent after it is in solution. However, many of the oxidation and substitution reactions become slower as the solvent polarity decreases.

2.2.1.7 GF

CAS Reg. No.: 329-99-7

Synonyms:

Cyclohexylmethylphosphonofluoridate
O-cyclohexyl-methylfluorophosphonate
EA 1212

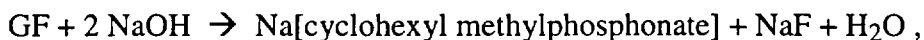
Properties: The nerve agent GF is a slightly volatile liquid, approximately 20 times more persistent than GB. It is almost insoluble in water. Table 2.16 presents the environmentally relevant properties of GF. The quality of the data presented in the table has not been evaluated.

TABLE 2.16 Environmentally Relevant Properties of GF

Property	Data	Reference
Empirical formula	C ₇ H ₁₄ FO ₂ P	Field Manual 3-9 ^a
Molecular weight	180.2 g/mol	Field Manual 3-9
Liquid density	1.1327 g/mL	Field Manual 3-9
Melting point	-30°C	Field Manual 3-9
Boiling point	239°C	Field Manual 3-9
Heat of vaporization	90.5 cal/g	Field Manual 3-9
Vapor pressure	0.044 mm Hg at 20°C	Field Manual 3-9
Log K _{OW}	Not available	Not available
Aqueous solubility	0.37% at 20°C	Field Manual 3-9
K _H (atm·m ³ /mol)	Not available	Not available
Diffusion coefficient (air) (cm ² /s)	Not available	Not available
Log K _{OC}	Not available	Not available
Volatility	438 mg/m ³ at 20°C 581 mg/m ³ at 25°C	Field Manual 3-9

^a Departments of Army, Navy, and Air Force (1990).

Reactions: Little information concerning reactions of GF was found. On the basis of similarities in structure to GB and GD, GF is expected to hydrolyze rapidly in alkaline solution according to the reaction:



where Na[cyclohexyl methylphosphonate] is the sodium salt of cyclohexyl methylphosphonic acid.

By comparison to GB and GD, the reaction is expected to be exothermic, and at pH 12 its half-life is expected to be in the range of the half-lives of GB (3 seconds) and GD (7 seconds) at that pH.

2.2.1.8 VX

CAS Reg. No.: 50782-69-9 (also 65143-05-7, 65167-63-7, 65167-64-8)

Synonyms:

Methyl-S-(2-bis(1-methylethylamino)ethyl) O-ethylphosphonothioic acid
 O-ethyl-S-(2-diisopropylaminoethyl) methylphosphonothioate
 S-2-diisopropylaminoethyl O-ethyl methylphosphonothioate
 S-2 (2-diisopropylamino)ethyl O-ethyl methylphosphonothioate
 O-ethyl-S-(2-diisopropylaminoethyl) methylthiolphosphonate
 EA 1701
 TX60

Properties: VX is more persistent than the G agents because of its lower vapor pressure. Its evaporation rate is about 1/1,500 that of water (Field Manual 3-9). Table 2.17 presents the environmentally relevant properties of VX.

Reactions: VX hydrolysis rates are slower than those of the G agents. For example, at pH 10 and 25°C, the half-life of VX in water is 40.5 hours (Epstein et al. 1974, cited in Rosenblatt et al. 1995), compared with 5 minutes for GB. The same source reported a half-life of 2.5 hours for the hydrolysis of VX in water at pH 12 at 25°C. At pH 5 and 25°C, the half-life of VX in water is 2,342 hours, compared with 160 hours for GB (Clark 1989, cited in Rosenblatt et al. 1995).

VX is not subject to acid-catalyzed hydrolysis but does undergo water-mediated and hydroxyl-ion-catalyzed hydrolysis. The hydrolysis of VX proceeds by multiple pathways and results in a more complex set of products than the hydrolysis of the G agents. Across the pH

TABLE 2.17 Environmentally Relevant Properties of VX

Property	Data	Data Quality	Reference
Empirical formula	C ₁₁ H ₂₆ NO ₂ PS	Not applicable	
Molecular weight	267.38 g/mol	Not applicable	
Liquid density	1.0083 g/mL at 25°C	Good	Samuel et al. 1983, cited in Rosenblatt et al. 1995
Melting point	-50°C	Fair	Samuel et al. 1983, cited in Rosenblatt et al. 1995
Boiling point	298.4°C	Good	Samuel et al. 1983, cited in Rosenblatt et al. 1995
Heat of vaporization	80.8 cal/g	Good	Samuel et al. 1983, cited in Rosenblatt et al. 1995
Vapor pressure (torr)	$6.2 \times 10^{-4}/25^{\circ}\text{C}$	Good	Samuel et al. 1983, cited in Rosenblatt et al. 1995
Log K _{OW}	2.36 (estimate)	Poor	Britton and Grant 1988, cited in Rosenblatt et al. 1995.
	2.09 (estimate)	Poor	Small 1984, cited in Rosenblatt et al. 1995.
	1.992 (estimate)	Poor	Sage and Howard 1989, cited in Rosenblatt et al. 1995.
Aqueous solubility	30 g/L at 25°C	Fair	Edgewood Arsenal 1974, cited in Rosenblatt et al. 1995
K _H (atm·m ³ /mol)	$7.2 \times 10^{-9}/25^{\circ}\text{C}$	Poor	Rosenblatt et al. 1995
Diffusion coefficient (air)	0.034 cm ² /s at 25°C	Fair	Samuel et al. 1983, cited in Rosenblatt et al. 1995
	0.062 cm ² /s at 300 K	Not available	U.S. Army 1999
Log K _{OC}	1.18	Poor	Sage and Howard 1989, cited in Rosenblatt et al. 1995.
	2.5	Not available	Small 1984, cited in Rosenblatt et al. 1995.

range, the P–S bond is cleaved to give two primary products: ethylmethylphosphonic acid (EMPA) and 2-diisopropylaminoethanethiol (DESH). Bis(2-diisopropylaminoethyl) disulfide (EA4196) is formed by air oxidation of DESH (Small 1984, cited in Rosenblatt et al. 1995). In the middle and higher pH ranges, additional reaction pathways contribute to the mix of hydrolysis products. In addition to P–S bond cleavage, the P–O–C bond to the ethoxy group and the C–S bond also are broken (Epstein et al. 1974, cited by Rosenblatt et al. 1995). The product of ethoxy group cleavage, EA2192, is comparatively stable toward hydrolysis (Sage and Howard 1989, cited in Rosenblatt et al. 1995). Yang and coworkers (1992) demonstrated that up to 13% EA2192 formed during the hydrolysis of VX even in aqueous 0.1 M NaOH. Szfraniec and coworkers (1993, cited in Rosenblatt et al. 1995) confirmed that 17% EA2192 formed in aqueous 2.0 M NaOH. Finally, C–S bond cleavage in the neutral pH range results in the formation of

O-ethyl methylphosphonothioic acid, diisopropylaminoethyl sulfide, and possibly other minor products (Epstein et al. 1974, and Yang et al. 1990, cited in Rosenblatt et al. 1995).

The NMR data presented by Durst and coworkers (1988) show the formation of EA2192 from VX in 10% alcoholic sodium hydroxide.

The chemical neutralization of VX also is complicated by its low solubility in water. It is a weak acid and therefore less soluble at higher pH, the region of faster reactions. At lower (more acidic) pH, the protonated form of VX is more soluble, but the reaction rate with water is much slower (Rosenblatt et al. 1995). The neutralization of VX has been investigated in a solution of 2 M NaOH with 10% isopropanol added to improve the solubility of VX. A 0.05 M solution of VX formed 22% EA2192 under those conditions (Yang et al. 1990 cited in Rosenblatt et al. 1995).

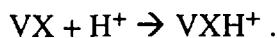
Further studies of the alkaline hydrolysis of a VX simulant (O, S-diethyl methylphosphonothioate) in very high concentrations of alcohol indicate that such solutions favor P-S bond cleavage rather than P-O-C bond cleavage. From this work with the simulant, it is inferred that VX could be neutralized rapidly without forming EA2192 in strongly basic solutions of methanol or propanol that contain less than 10% water. This effect has been attributed to the hydrolysis of VX by the preponderance of alkoxide ion present, not to the decreased solvent polarity (Yang et al. 1993b, cited in Rosenblatt et al. 1995).

Because of the sensitivity of VX to hydrolysis, its decomposition in munitions has been a problem. N,N'-diisopropylcarbodiimide and N,N'-dicyclohexylcarbodiimide have been added as stabilizers to weapons grade VX (Rosenblatt et al. 1995). Hydrolysis converts these stabilizers to N,N'-diisopropylurea or N,N'-dicyclohexylurea, respectively (Rosenblatt et al. 1995).

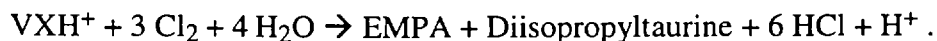
The products of the reaction of aqueous hypochlorite with VX vary with pH. At low pH, hypochlorous acid reacts with chloride ion to form chlorine:



Also at low pH, the VX is protonated on the nitrogen, enhancing its solubility:



The chlorine reacts with the protonated VX to form EMPA and a sulfonic acid:



This reaction is thought to proceed in two steps. First the sulfur atom is oxidized, then the P–S bond is cleaved by hydrolysis to yield the products (Yang et al. 1992).

At higher pH, the nitrogen atom in VX is not protonated. The OCl^- is thought to attack the available nitrogen, forming an N-oxide, and then oxidize the sulfur atom (Yang et al. 1992). However, the reactions of hypochlorite with VX in basic solution have not been completely defined. Durst and coworkers (1988) noted the possibility of toxic products forming at a pH below 11. With sufficient excess hypochlorite, the stoichiometry of the reaction has been reported (Durst et al. 1988) as:



2.2.1.9 Vx

CAS Reg. No.: 159939-87-4

Synonyms:

S-2(2-diethylamino)ethyl O-isobutyl methylphosphonothioate

Methylphosphonothioic acid, S-[2-(diethylamino)ethyl] O-2-methylpropyl ester

V gas

Russian VX

Properties: Vx (called “V sub x”) is a V agent with properties similar to VX. The limited information available on this compound is presented in Table 2.18.

Reactions: The chemical neutralization reactions of Vx are expected to be similar to those of VX (Field Manual 3-9).

TABLE 2.18 Environmentally Relevant Properties of Vx

Property	Data	Reference
Empirical formula	$\text{C}_{11}\text{H}_{26}\text{NO}_2\text{PS}$	
Molecular weight	267.38 g/mol	ChemFinder

2.2.1.10 H/HD (Sulfur Mustard)

CAS Reg. No.: 505-60-2

Synonyms:

Bis(2-chloroethyl) sulfide
 Bis(beta-chloroethyl) sulfide
 1-Chloro-2 (beta-chloroethylthio) ethane
 Beta, beta' - dichlorodiethyl sulfide
 2,2'-Dichlorodiethyl sulfide
 Di-2-chloroethyl sulfide
 Beta, beta' - dichloroethyl sulfide
 2,2' - Dichloroethyl sulfide
 EA 1033
 Iprit
 Kampstoff "Lost"
 Levinstein
 Lost
 Mustard gas
 Senfgas
 S-lost
 Sulphur mustard gas
 S-yperite
 Yellow cross liquid
 Yperite

Properties: The two common mustard agents are:

- H (Levinstein mustard): 70% bis(2-chloroethyl) sulfide with 30% sulfur-based impurities and
- HD (distilled mustard): bis(2-chloroethyl) sulfide.

H was synthesized for military use mainly by the Levinstein process. In its simplest form, the Levinstein process is a reaction between sulfur monochloride and ethylene to produce mustard and elemental sulfur:



This reaction is complicated by the fact that most of the elemental sulfur reacts to form a variety of polysulfides. The Levinstein process produces mustard in a 70% yield, with the

proportions of sulfur and the polysulfide impurities depending upon reaction conditions (Rosenblatt et al. 1995).

The sulfur impurities gave H a distinct odor. They also lowered its freezing point a few degrees, but caused problems with storage. Therefore, a purification process consisting of washing and vacuum distillation was used to produce HD from H (Field Manual 3-9). No listing has been found for the composition of a "typical" sample of H. Such a listing may not be available. Rosenblatt and coworkers (1995) reported the results from analysis of mustard from two old H munitions and a storage container of HD. Because HD is distilled from H, the two mustards are often referred to as H/HD, particularly when discussing properties and reactions.

HD has a low solubility in water and a low rate of solution. However, once HD is dissolved in water, it hydrolyzes rapidly. The hydrolysis of mustard proceeds via an S_N1 mechanism, very likely through a cyclic sulfonium ion intermediate (Yang et al. 1992). Table 2.19 presents the environmentally relevant properties of HD.

Reactions: The nature of the hydrolysis products of HD is highly dependent on the reaction conditions. Under ideal conditions (a large excess of water, high pH, and adequate stirring), HD can be hydrolyzed almost exclusively to thiodiglycol and chloride ion (Rosenblatt et al. 1995). With a HD to water ratio of 1 to 2.5 and a high pH, 1,4-oxathiane, 1,4-dithiane, 2-vinylthioethanol, and mustard chlorohydrin formed, in addition to polysulfides and some uncharacterized compounds (D'Agostino and Provost 1985, cited in Rosenblatt et al. 1995). Bulk HD can persist deep in the soil or under quiescent water for years (Rosenblatt et al. 1995). This persistence is thought to be a result of the presence of a layer of oligomeric polysulfide degradation products formed by limited hydrolysis (Rosenblatt et al. 1995). In one experiment, equal volumes of HD and water were allowed to stand. After two months, at least 50% of the original HD phase still was present. NMR data indicated that the most abundant product was the large ion, H-2TG, with lesser amounts of H-TG and CH-TG. Evidence exists that these ions could revert back to HD (Yang et al. 1992). Therefore, alkaline hydrolysis is rarely used to neutralize HD.

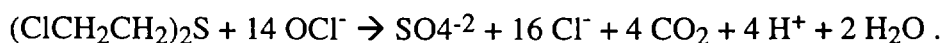
Organic solvents have been added to mustard neutralization solutions to solubilize the HD and increase the effective rate of hydrolysis. Often these solvents suppress the formation of the sulfonium ion intermediate, thereby reducing the effective rate of HD hydrolysis. The addition of 5% acetone to HD in water was found to double the half-life of HD in water (Yang et al. 1986, cited in Rosenblatt et al. 1995).

Because the sulfur atom in HD can be oxidized, oxidation is an important approach to the chemical neutralization of mustard. Hypochlorite bleaches have been used for this purpose. The reaction depends upon the proportions of reactants and temperature. It is thought to proceed through formation of the sulfoxide and the sulfone of HD, followed by a series of elimination reactions (Rosenblatt et al. 1995). Under optimum conditions (excess chemical neutralization

TABLE 2.19 Environmentally Relevant Properties of HD

Property	Data	Data Quality	Reference
Empirical formula	C ₄ H ₈ Cl ₂ S	Not applicable	
Molecular weight	159.08 g/mol	Not applicable	
Liquid density	1.2685 g/mL at 25°C	Good	Samuel et al. 1983, cited in Rosenblatt et al. 1995
Melting point	14.445°C	Good	Penski 1993, cited in Rosenblatt et al. 1995
Boiling point	217.5°C	Good	Samuel et al. 1983, cited in Rosenblatt et al. 1995
Heat of vaporization	94.3 cal/g	Good	Samuel et al. 1983, cited in Rosenblatt et al. 1995
Vapor pressure (torr)	0.082/22°C	Good	Samuel et al. 1983, cited in Rosenblatt et al. 1995
	0.1059/25°C	Good	Samuel et al. 1983, cited in Rosenblatt et al. 1995
	0.11/25°C	Not available	Edgewood Arsenal 1974
	0.165	Not available	MacNaughton and Brewer 1994
	1.37	Good	Rosenblatt et al. 1995
Log K _{OW}	2.026	Fair	Sage and Howard 1989, cited in Rosenblatt et al. 1995
Aqueous solubility	0.92 g/L at 22°C	Fair	Edgewood Arsenal 1974, cited in Rosenblatt et al. 1995
K _H (atm·m ³ /mol)	1.87 x 10 ⁻⁵	Fair	Rosenblatt et al. 1995
	2.57 x 10 ⁻⁵	Fair	Sage and Howard 1989, cited in Rosenblatt et al. 1995
Diffusion coefficient (air)	0.060 cm ² /s at 25°C	Fair	Samuel et al. 1983, cited in Rosenblatt et al. 1995
	0.099 cm ² /s at 300 K	Not available	U.S. Army 1999
Log K _{OC}	2.0-2.1	Poor	Sage and Howard 1989, cited in Rosenblatt et al. 1995

reagent, high pH, and adequate stirring), hypochlorite will oxidize HD to sulfate, chloride, and carbon dioxide according to the following equation:



The ¹³C NMR analysis of one such reaction mixture revealed more than 99.5% destruction of HD and the formation of about 20 uncharacterized carbon-containing products. With a deficiency of hypochlorite, the sulfoxide and/or the sulfone of HD may persist

(Durst et al. 1988). Oxidation is favored in basic solutions of hypochlorite and HD; in neutral or acidic solutions, chlorination occurs (Rosenblatt et al. 1995).

Little is known about the effect of hypochlorite upon the impurities produced during the manufacture of H/HD. It is likely that conditions favorable to the complete mineralization of HD to sulfate, chloride and carbon dioxide also will oxidize the additional sulfur atoms in the polysulfides. Other sulfur-containing impurities probably would be oxidized as well, if not to sulfate, at least to sulfoxides, sulfones or sulfonic acids (Rosenblatt et al. 1995).

2.2.1.11 HT

CAS Reg. No.: Not available for HT; for agent T: 63918-89-8. (HT is a mixture of 60% HD and 40% T [another blister agent].)

Synonyms (for agent T):

Bis-[2-(2-chloroethylthio)]ethyl ether
Di-[2-(2-chloroethylthio)]ethyl ether
Di-[2-(B-chloroethyl thio)]ethyl ether

Properties: Agent T is a mustard, but it was not used as a separate filling in munitions. It was mixed with HD to lower the melting point of the HD (Dugway Proving Ground 1978). Table 2.20 presents the environmentally relevant properties of HT. The quality of the data presented in this table has not been evaluated.

Reactions: Although T has not been studied as a separate agent, its structure is very similar to that of HD, and its chemistry is expected to be very similar to that of HD (Durst et al. 1988).

2.2.1.12 HQ

CAS Reg. No.: Not Available for HQ; for agent Q: 3563-36-8. (HQ is a mixture of HD and another blister agent designated as Q. The usual mixture is 75% HD and 25% Q [Safety Office 1995].)

Synonyms (for Agent Q):

Sulfur sesquimustard
1,2-bis(2-chloroethylthio)ethane
Doppel-Q
Sesqua yperite

TABLE 2.20 Environmentally Relevant Properties of HT

Property	Data	Reference
Empirical formula	HD: C ₄ H ₈ Cl ₂ S T: C ₈ H ₁₆ Cl ₂ OS ₂	Field Manual 3-9 ^a
Molecular weight	HD: 159.08 g/mol T: 263.3 g/mol HT: 189.4 g/mol (average based on 60:40 weight percent)	Field Manual 3-9
Liquid density	1.269 g/cm ³ at 25°C	Field Manual 3-9
Melting point	0.0 to 1.3°C (60/40 mixture)	Field Manual 3-9
Boiling point	Above 228°C	Field Manual 3-9
Heat of vaporization	Not available	Not available
Vapor pressure	0.104 mm Hg at 25°C	Field Manual 3-9
Log K _{OW}	Not available	Not available
Aqueous solubility (g/L)	Barely soluble in water.	Field Manual 3-9
K _H (atm-m ³ /mol)	Not available	Not available
Diffusion coefficient (air) (cm ² /s)	Not available	Not available
Log K _{OC}	Not available	Not available
Volatility	831 mg/m ³ at 25°C	Field Manual 3-9

^a Departments of the Army, Navy, and Air Force (1990).

Properties: Agent Q is used exclusively in a mixture with HD to increase persistence. Q is the most powerful known military vesicant on bare skin, but it has a low vapor pressure and cannot form a vapor threat. Table 2.21 presents the environmentally relevant properties of HQ. The quality of the data presented in this table has not been evaluated.

Reactions: The structure of agent Q is closely related to that of HD; therefore, the reactions of agent Q are expected to be similar to those of HD.

TABLE 2.21 Environmentally Relevant Properties of HQ

Property	Data	Reference
Empirical formula	HD: C ₄ H ₈ Cl ₂ S T: C ₆ H ₁₂ Cl ₂ S ₂	Field Manual 3-9 ^a Safety Office 1995
Molecular weight	HD: 159.08 g/mol Q: 219.13 g/mol	Field Manual 3-9 Safety Office 1995
Liquid density	Not available	Not available
Melting point	Not available	Not available
Boiling point	Not available	Not available
Heat of vaporization	Not available	Not available
Vapor pressure	0.088 @ 25°C (calculated)	Safety Office 1995
Log K _{OW}	Not available	Not available
Aqueous solubility (g/L)	Not available	Not available
K _H (atm-m ³ /mol)	Not available	Not available
Diffusion coefficient (air) (cm ² /s)	Not available	Not available
Log K _{OC}	Not available	Not available
Volatility	0.0822 mg/m ³ at 25°C	Safety Office 1995

^a Departments of the Army, Navy, and Air Force (1990).

2.2.1.13 L (Lewisite)

CAS Reg. No.: 541-25-3

Synonyms:

(2-Chlorovinyl) dichloroarsine
 (2-Chloroethenyl) arsonous dichloride
 Chlorovinylarsine dichloride
 2-Chlorovinyl dichloroarsine
 Beta-chlorovinyl dichloroarsine
 Dichloro (2-chlorovinyl) arsine
 EA 1034

Properties: L is an arsenical vesicant produced for use in World War II. Stored L contains four substances; L1, 2-chlorovinyl dichloroarsine, is the primary component. L2, bis-(2-chlorovinyl) dichloroarsine, also is a vesicant and may be present up to 10% or 20%. Some arsenic trichloride (AsCl₃) is also present (Yurow and Davis 1982). L3, tris(2-chlorovinyl)arsine is present as an impurity in stored L. It is not a vesicant (Jackson and Jackson 1935). Table 2.22

TABLE 2.22 Environmentally Relevant Properties of L

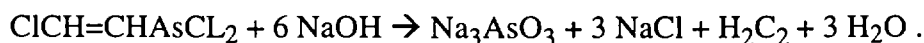
Property	Data	Reference
Empirical formula	C ₂ H ₂ AsCl ₃	Field Manual 3-9 ^a
Molecular weight	207.35 g/mol	Field Manual 3-9
Liquid density	1.89 g/mL at 20°C	Field Manual 3-9
Melting point	-18°C	Field Manual 3-9
Boiling point	190°C 195.9°C	Field Manual 3-9 Samuel et al. 1983
Heat of vaporization	58 cal/g from 0°C to 190°C	Field Manual 3-9
Vapor pressure	0.087 mm Hg at 0°C 0.394 mm Hg at 20°C 0.58 mm Hg at 25°C	Field Manual 3-9 Edgewood Arsenal 1974
	0.40 (trans)	U.S. Army 1999
	1.56 (cis)	U.S. Army 1999
Log K _{OW}	Not available	Not available
Aqueous solubility (g/L)	0.5 ^b	Rosenblatt et al. 1975
K _H (atm·m ³ /mol)	Not available	Not available
Diffusion coefficient (air) (cm ² /s)	0.099	U.S. Army 1999
Log K _{OC}	Not available	Not available
Volatility	4.48 × 10 ³ mg/m ³ at 20°C	Field Manual 3-9

^a Departments of the Army, Navy, and Air Force (1990).

^b According to Rosenblatt et al. (1975), solubility data for lewisite are meaningless because of very rapid hydrolysis, which is limited by slow rate of dissolution.

lists the environmentally relevant properties of L. The quality of the data presented in the table has not been evaluated.

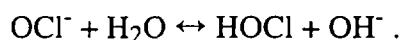
Reactions: When subjected to basic solutions, L decomposes to arsenite, chloride, and acetylene according to the following equation:



Yurow and Davis (1992) report this reaction to be complete in less than 10 seconds with a heat of reaction of -102,000 cal/mol. L-2 appears to decompose more slowly in aqueous sodium hydroxide than does L-1. L-2 in chloroform has been chemically neutralized with aqueous sodium hydroxide.

Durst and coworkers (1988) cited a report by Bartlett (1942) that the cis and trans isomers of L react at different rates in 16% sodium hydroxide, but the reaction for both isomers was found to be complete in approximately 1 hour. Hewitt (1948) reported that the manufacture of L with an AlCl_3 catalyst produces 100% trans-L, while the use of HgCl_2 or CuCl catalysts results in a mixture of 90% trans and 10% cis isomers. The cis isomer was the slower of the two to react with base. Hewitt also noted that the cis isomer dissolved in cold NaOH without the evolution of acetylene and formed vinyl chloride when the solution was warmed to 40°C . Smith and coworkers (1993) reported the analysis of a sample of distilled L. They found 95% trans isomer, <2% cis isomer, and 3% of a geminal isomer that had the chlorine attached to the carbon atom that was bonded to arsenic. The presence of the geminal isomer may explain the behavior of Hewitt's "cis isomer." Waters and Williams (1950) reported that to form acetylene, at 16°C the pH of a solution of L must be at least 10.5 and at 50°C must be at least 9. Because of the relative insolubility of L and its oxide in aqueous solutions, the use of a cosolvent such as an alcohol has been recommended (Durst et al. 1988).

Durst and coworkers (1988) cited a report by Buswell and Price (1944) that the reaction of L with hypochlorite has been studied, but because of the relatively slow kinetics of oxidation in solution, it offers no advantage over aqueous sodium hydroxide. According to Durst and coworkers (1988), the reaction of L with hypochlorite in aqueous solution proceeds as an alkaline hydrolysis, producing arsenate, chloride, and acetylene, with the hypochlorite serving as a source of hydroxide according to the following equilibrium:



Davis et. al. (1979) noted that L reacts with dry STB with the liberation of chlorine. Another report (Mcandless and Fedor 1992) described a three-step process for the chemical neutralization of L. It consisted of conversion of L to lewisite oxide by addition of the agent to aqueous caustic hydrogen peroxide under controlled pH conditions, followed by removal of excess peroxide, and then conversion of the lewisite oxide to arsenate and chloride salts. No additional details were given.

In H_2O , L reacts rapidly to give lumps that are soluble only upon prolonged stirring and are polymeric modifications of lewisite oxide, ClCH=CHAsO . The degree of polymerization of the residue depends upon age. Oxidation of lewisite oxide to the pentavalent state markedly reduces its toxicity (Yurow and Davis 1982).

In 1991, Chem-Security Ltd. developed a three-step neutralization process to destroy the Canadian stockpile of lewisite. Lewisite is converted to sodium arsenate in this process. CAMDS has received a RCRA RD&D permit for this process, with operation scheduled to begin in early 1999. Details of this neutralization process may be found in the RD&D permit, available for review in DSHW's public information office.

2.2.1.14 HL

CAS Reg. No.: Not available.

Synonym:

Sulfur mustard/lewisite

Properties: HL is a variable combination of HD and L that provides a mixture of low freezing point for use in cold weather operations or high-altitude spray. Table 2.23 presents the environmentally relevant properties for the eutectic mixture (37% HD, 63% L by weight), which has the lowest possible freezing point (Field Manual 3-9). The quality of the data presented in the table has not been evaluated.

TABLE 2.23 Environmentally Relevant Properties of HL

Property	Data	Reference
Empirical formula	HD: $C_4H_8Cl_2S$ L: $C_2H_2AsCl_3$	Field Manual 3-9 ^a
Molecular weight	HD: 159.08 g/mol L: 207.35 g/mol	Field Manual 3-9
Eutectic mixture (37% HD/63%L)	186.4 g/mol	
Liquid density	Approx. 1.66 g/mL at 20°C	Field Manual 3-9
Melting point		Material Safety Data Sheet for HL
purified agent mix:	-25.4°C	
typical production batch:	-42°C	
Boiling point	Indefinite, but below 190°C	Field Manual 3-9
Heat of vaporization	Between HD and L	Field Manual 3-9
Vapor pressure	0.248 mm Hg at 20°C (calculated)	Field Manual 3-9
Log K_{OW}	Not available	Not Available
Aqueous solubility (g/L)	Practically insoluble	Material Safety Data Sheet for HL
K_H (atm-m ³ /mol)	Not available	Not available
Diffusion coefficient (air) (cm ² /s)	Not available	Not available
Log K_{OC}	Not available	Not available
Volatility	2,730 mg/m ³ at 20°C (calculated)	Field Manual 3-9

^a Departments of the Army, Navy, and Air Force (1990).

Reactions: The chemical neutralization of HL is expected to proceed as parallel neutralizations of HD and L and to produce a mixture of neutralization products from the two processes.

2.2.1.15 HN1

CAS Reg. No.: 538-07-8

Synonyms:

Bis(2-chloroethyl)ethylamine

Ethylbis(2-chloroethyl)amine

Nitrogen Mustard (HN1)

Ethyl S

HN-Lost

Properties: HN1 is a vesicant similar to HD in its properties and effects, but only one-fifth as damaging and not as stable. It is more volatile, and therefore less persistent, than HD (Field Manual 3-9). Table 2.24 presents the environmentally relevant properties of HN1. The quality of the data presented in this table has not been evaluated.

TABLE 2.24 Environmentally Relevant Properties of HN1

Property	Data	Reference
Empirical formula	$C_6H_{13}Cl_2N$	Field Manual 3-9 ^a
Molecular weight	170.08 g/mol	Field Manual 3-9
Liquid density	1.09 g/mL at 25°C	Field Manual 3-9
Melting point	-34°C	Field Manual 3-9
Boiling point	194°C (calculated; decomposes)	Field Manual 3-9
Heat of vaporization	77 cal/g	Field Manual 3-9
Vapor pressure	0.24 mm Hg at 25°C	Field Manual 3-9
Log K_{OW}	Not available	Not available
Aqueous solubility (g/L)	Sparingly soluble in water	Field Manual 3-9
K_H (atm·m ³ /mol)	Not available	Not available
Diffusion coefficient (air) (cm ² /s)	Not available	Not available
Log K_{OC}	Not available	Not available
Volatility	308 mg/m ³ at 0°C 1,520 mg/m ³ at 20°C	Field Manual 3-9

^a Departments of the Army, Navy, and Air Force (1990).

Reactions: The nitrogen mustards hydrolyze in water to give products related to the formation of an aziridinium (or ethyleneimmonium) ion. Therefore, basic solutions are preferred for chemical neutralization. The hydrolysis half-life of HN1 in dilute sodium hydroxide was described as being 12 minutes at 18°C, but the overall neutralization rate was limited by the low solubility of HN1. Some chemical neutralization work has been reported using monoethanolamine. The only information found concerning aqueous oxidative neutralization of the nitrogen mustards was a reference to some exploratory studies (Yurow and Davis 1982).

2.2.1.16 HN3

CAS Reg. No.: 555-77-1

Synonyms:

Tris(2-chloroethyl)amine
2,2',2''-Trichlorotriethylamine
Tri(2-chloroethyl)amine
Nitrogen Mustard (HN3)

Properties: HN3 is the principal representative of the nitrogen mustards because it has vesicant properties almost equal to those of HD. It is more persistent than HD. It also is the most stable in storage of the three nitrogen mustards (Field Manual 3-9). Table 2.25 presents the environmentally relevant properties of HN3. The quality of the data presented in this table has not been evaluated.

Reactions: The reactions of HN3 are expected to be similar to those of HN1.

2.2.2 Chemical Neutralization Solutions

This section discusses chemical neutralization solution reactions (Section 2.2.2.1) and spent chemical neutralization solutions (Section 2.2.2.2).

2.2.2.1 Chemical Neutralization Solution Reactions

According to Durst and coworkers (1988), the term “hydrolysis” refers to the addition of water to a reactive molecule, with the elimination of some fragment of the reactive molecule into the aqueous solution. For example, water will react with GB according to the following equation:

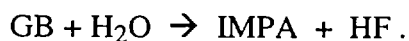


TABLE 2.25 Environmentally Relevant Properties of HN3

Property	Data	Reference
Empirical formula	C ₆ H ₁₂ Cl ₃ N	Field Manual 3-9 ^a
Molecular weight	204.54 g/mol	Field Manual 3-9
Liquid density	1.24 g/mL at 25°C	Field Manual 3-9
Melting point	-3.7°C	Field Manual 3-9
Boiling point	256°C (calculated; decomposes)	Field Manual 3-9
Heat of vaporization	74 cal/g	Field Manual 3-9
Vapor pressure	0.0109 mm Hg at 25°C	Field Manual 3-9
Log K _{OW}	Not available	Not available
Aqueous solubility (g/L)	Insoluble in water	Field Manual 3-9
K _H (atm-m ³ /mol)	Not available	Not available
Diffusion coefficient (air) (cm ² /s)	Not available	Not available
Log K _{OC}	Not available	Not available
Volatility	13 mg/m ³ at 0°C 121 mg/m ³ at 25°C 180 mg/m ³ at 30°C	Field Manual 3-9

^a Departments of the Army, Navy, and Air Force (1990).

The concept of hydrolysis includes the reactions of the ions of water, which are OH⁻ and H⁺. These reactions are referred to as alkaline and acid hydrolysis, respectively. If OH⁻ is added to a solution containing GB, the alkaline hydrolysis reaction is very rapid. In the case of GB, the anion of IMPA and the fluoride ion are formed. The reaction of GB with water is too slow to be practical as a chemical neutralization procedure. However, the reaction of GB with hydroxide ion is a very effective approach to the chemical neutralization of that chemical agent. More OH⁻ is consumed in the alkaline hydrolysis of GB because additional hydroxide is used to neutralize the acid products formed. The equation for the alkaline hydrolysis of GB is as follows:



where Na[IMPA] is the sodium salt of IMPA.

GB will undergo alkaline hydrolysis in the same way without regard to the source of OH⁻. Thus, GB will hydrolyze to produce the same organic anion product, IMPA, when reacted

with NaOH, Na₂CO₃, or NH₄OH because all are sources of hydroxide ion in aqueous solution. For example, Na₂CO₃ forms hydroxide in aqueous solution according to the following equation:



Different sources of OH⁻ are employed because in many deliberate chemical neutralization situations, military units have a need to reuse the neutralized item. NaOH corrodes equipment made of aluminum and magnesium. Therefore, Na₂CO₃ often is used to chemically neutralize reusable items made from such materials because it does not corrode them. NH₄OH also is a weaker source of hydroxide ion than NaOH because it is only partially ionized to ammonium and hydroxide ions. Table 2.26 lists approximate pH values for various concentrations of bases used for alkaline hydrolysis of chemical agents – the higher the pH, the higher the hydroxide concentration (Durst et al. 1988).

NaOH is comparatively inexpensive and offers the highest pH at a particular concentration; therefore, in the absence of other considerations it often is chosen as the source of hydroxide ion for chemical agent waste neutralization by alkaline hydrolysis.

The chemical agents undergo the same oxidation reactions with hypochlorite ion whether the ion comes from NaOCl, STB, or HTH. The use of hypochlorite in chemical neutralization of mustard and VX depends upon the oxidative action of hypochlorite upon sulfur in mustard and upon nitrogen and sulfur in VX. When more than a small quantity of agent is oxidized, the reaction is vigorous, and care must be taken to control the rate at which heat is produced. A lower concentration of chemical neutralization solution may be used or the rate of addition of agent to the neutralization solution may be controlled to moderate the oxidation reaction.

Apart from its oxidative capability, hypochlorite also can function as a nucleophile, hydrolyzing G agents in a way similar to the hydroxide ion. The normal hydroxide ion hydrolysis products from the G agents also are produced by hypochlorite ion. In the case of GA, the dimethylamino group is lost in addition to the cyano group (Durst et al. 1988).

TABLE 2.26 Approximate pH Values of Solutions of Various Concentrations of Selected Bases

Base	pH in 0.1 N Base	pH in 0.01 N Base
NaOH	13.1	12.1
Na ₂ CO ₃	11.5	11.0
NH ₄ OH	11.3	10.8

2.2.2.2 Spent Chemical Neutralization Solutions

Although a number of different solutions are used for chemical neutralization, the reactions that achieve neutralization of the chemical agents fall into two categories: hydrolysis or oxidation. The concentration, but not the chemical source, of the hydroxide or hypochlorite ions determines the reaction pathways and the rates of the neutralization reactions with the chemical agents. A variety of compounds remain in the chemical neutralization solutions after use.

Hypochlorite solutions that have stood for any length of time may contain chlorate ion as a contaminant because of the disproportionation equilibrium shown by the following equation (Bodek et al. 1988, cited in Rosenblatt et al. 1995):



Fluoride ion results from the chemical neutralization of GB, GD, and GF. Alkyl methylphosphonic acids result from the neutralization of the G agents and VX. Thiodiglycol is the product of the complete hydrolysis of mustard. The alkaline chlorinolysis of VX produces alkyl phosphonic acid and diisopropylamine. Tributylamine, sometimes added to GB, is unaffected by hydrolysis. It probably would be oxidized to dibutylamine and butyraldehyde by hypochlorite (Rosenblatt et al. 1995). Cyanide ion is formed when GA is neutralized with aqueous hydroxide. It may be necessary to treat the solution with hypochlorite to convert the cyanide to nitrogen gas and carbonate ion (Yurow 1988). Solutions resulting from the hydrolysis of L contain arsenite ion (AsO_3^{-3}) or arsenate ion (AsO_4^{-3}).

The stabilizers N,N'-diisopropylcarbodiimide and N,N'-dicyclohexylcarbodiimide are hydrolyzed to the respective ureas. Under conditions of chlorinolysis, the ureas could become N,N'-dichlorinated.

Under some circumstances, organic solvents (alcohol, acetone) remain after being added to solubilize agents such as thickened GD, HD, or VX. In other situations, solutions of chemical agents in solvents such as chloroform or carbon tetrachloride are neutralized, and the residual solvents become part of the waste stream.

Under dehydrating conditions, the alkyl methyl phosphonates from the hydrolysis of G agents and VX can form anhydrides. This is not expected to occur in aqueous solutions. It is highly unlikely that VX, once hydrolyzed, would reform under any conditions. One of the major hydrolysis products of VX, diisopropylaminoethanethiol, can be air oxidized to a reputedly vesicant disulfide (Rosenblatt et al. 1995).

3 SUPPORT FOR CHEMICAL NEUTRALIZATION OF CHEMICAL AGENT WASTE STREAMS AS APPLICABLE AND DEMONSTRATED TREATMENT TECHNOLOGIES

The purpose of this section is to support chemical neutralization as an applicable LDR treatment technology on the basis of demonstration data. To be considered applicable, a technology must theoretically be capable of treating either the waste in question or a waste that is similar in terms of the parameters that affect the selection of the treatment methods. Parameters that affect treatment performance may include both physical and chemical characteristics, such as pH, bond disassociation energy, thermal conductivity, inorganic and organic composition, and concentration of the constituents of concern.

To be considered demonstrated, a technology must be employed in operation for the treatment of the waste in question or a similar waste. Technologies may also be considered demonstrated for wastes with similar parameters (such as similar physical and chemical characteristics) that affect treatment performance.

To support the chemical neutralization of chemical agent related waste streams as applicable and demonstrated treatment technologies, this section presents the following topics:

- Applicability of chemical neutralization as a treatment technology
- Performance database

3.1 APPLICABILITY OF CHEMICAL NEUTRALIZATION AS A TREATMENT TECHNOLOGY

Chemical neutralization procedures used are evaluated as applicable on the basis of the following categories: general chemistry, nuclear magnetic resonance (NMR) data, thermodynamics and kinetics of the reaction, and the re-formation of chemical agent from chemical neutralization products. The chemical reactions involved in the chemical neutralization procedures used have been studied extensively, and a large amount of data have been gathered. General chemistry is described in Section 2. Descriptions of the other categories are presented here.

NMR evidence is significant because it provides unambiguous information regarding disappearance of the chemical agent and appearance of the chemical neutralization products in the same reaction mixture at the same time. It also provides information on how "clean" a neutralization reaction is, that is, the number of side products and their approximate concentrations. The NMR measurements reviewed in this report have a detection limit of

approximately 0.5%. Therefore, components present at less than 0.5% do not appear in the NMR spectra referenced in this discussion (Durst et al. 1988).

The equilibrium constant for a reaction (K_{eq}) can be calculated from the change in free energy of the reaction according to the relationship:

$$\Delta G = -2.303 RT \log K_{eq} ,$$

where

ΔG = the change in free energy ($G_{products} - G_{reactants}$),

R = the gas constant, and

T = the absolute temperature.

A large negative change in free energy corresponds to an equilibrium constant that favors the products of the reaction. The free energy of a reaction is related to the heat of reaction by the equation:

$$\Delta G = \Delta H - T\Delta S ,$$

where

ΔH = the heat of reaction, or change in enthalpy ($H_{products} - H_{reactants}$),

T = the absolute temperature, and

ΔS = the change in entropy ($S_{products} - S_{reactants}$).

If the products and reactants both remain in solution, the entropy term, $T\Delta S$, usually does not change by a large amount. This condition leads to the general observation that an exothermic reaction that has a large negative ΔH will have a negative ΔG term, indicating an equilibrium favoring the products.

The chemical agent neutralization reactions are exothermic, in some instances very exothermic. By using the equations given above and tables of thermodynamic values, it is possible to estimate the free energies of reactions and their corresponding equilibrium constants. This has been done for the alkaline hydrolysis of GB in the following equation:



The $\Delta H = -44,400$ cal/mol (Davis et al. 1977). The ΔG has been calculated to be $-30,000$ cal/mol, and the resulting equilibrium constant is estimated at $\log K_{eq} = 21.9$, indicating a very strong tendency to favor completion of the reaction (Durst et al. 1988).

Free energy of a reaction must be negative for the reaction to proceed. However, a negative free energy does not guarantee that a reaction will proceed; non-thermodynamic factors also significantly affect reaction rates. Thermodynamic predictions must be evaluated in light of measured reaction rate data. Generally, the chemical agent neutralization reactions are exothermic, and generally the recommended chemical neutralization reactions proceed rapidly in solution. The principal non-thermodynamic factor that requires consideration in chemical neutralization processes is agent solubility in water. HD and VX, for example, are less than 1% soluble in water at room temperature (Field Manual 3-9 [Departments of the Army, Navy, and Air Force 1990]). The thermodynamics and kinetics of each agent/neutralization reaction are discussed below. Table 3.1 presents heats of reaction and half-lives for chemical reactions resulting from the chemical neutralization procedures.

TABLE 3.1 Thermochemical and Kinetic Data

Chemical Agent	Chemical Neutralization Solution	Heat of Reaction	Half-Life	Reference
GA	Water, pH 9.5	Not available	35 min/25°C	Yurow and Davis 1982
GA	Aqueous OH ⁻ , pH 12	Not available	9.2 s	Durst et al. 1988
GA	Sodium hydroxide	-10.1 kcal/mol	Not available	Yurow and Davis 1982
GB	Sodium hydroxide	-44.4 kcal/mol	Not available	Yurow and Davis 1982
GB	5% Sodium hydroxide	Not available	< 0.8 s/25°C	Yurow and Davis 1982
GB	10% Sodium carbonate	-22 kcal/mol	8.5 s/25°C	Yurow and Davis 1982
GB	Water, pH 10	Not available	~ 4 min/25°C	Yurow and Davis 1982
GB	Water, pH 10	Not available	5 min/25°C	Demek et al. 1970, cited in Rosenblatt et al. 1995
GB	5% Alkaline bleach	Not available	Instantaneous/25°C	Yurow and Davis 1982
GD	5% Sodium hydroxide	Not available	0.08 h/20°C	Yurow 1988
VX	Alkaline hypochlorite	Approx. -700 kcal/mol	Not available	Yurow and Davis 1982
VX	10% HTH slurry	Not available	~ 70 s/25°C	Yurow and Davis 1982
VX	Water, pH 14	Not available	1.3 min/25°C	Yurow and Davis 1982
VX	Water, pH 12	Not available	2.5 h/25°C	Epstein, et al. 1974, cited in Rosenblatt et al. 1995
HD	Alkaline hypochlorite	Highly exothermic	Not available	Yurow and Davis 1982
L	Sodium hydroxide	-102 kcal/mol	Not available	Yurow and Davis 1982
L	5% Sodium hydroxide	Not available	Instantaneous/25°C	Yurow and Davis 1982
L	Water	Not available	Very fast/25°C	Yurow and Davis 1982
HN1	Dil. sodium hydroxide	Not available	12 min/18°C	Yurow and Davis 1982

In general, there is no evidence to support re-forming of agent in dilute, unmodified chemical neutralization solutions. However, when the products of chemical neutralization are concentrated or modified, there is a possibility that some agents could re-form.

The principal chemical reaction(s) for each agent/neutralization solution pair used is described in the following sections. The presence of impurities and additives are identified and their reactions are discussed.

3.1.1 Chemical Neutralization of GB by Alkaline Hydrolysis

GB is miscible with water (Field Manual 3-9). GB is routinely neutralized with 10 to 18% aqueous NaOH, 10% NaOH in alcohol, 10% aqueous Na₂CO₃, and concentrated NH₄OH. This discussion applies specifically to the chemical neutralization of GB in 10% aqueous NaOH. It applies generally to the following three additional procedures: GB in 10% NaOH in alcohol, GB in 10% aqueous Na₂CO₃, and GB in concentrated NH₄OH.

The chemical neutralization of GB in sodium hydroxide proceeds by the following reaction:



where

Na[IMPA] = the sodium salt of IMPA and

NaF = sodium fluoride.

The ³¹P NMR evidence indicates that greater than 99.5% GB proceeds to greater than 99.5% Na[IMPA], with phosphorus-containing side products constituting less than 0.5%. Similar NMR results have been reported for the chemical neutralization of GB in 10% NaOH in alcohol and in 10% aqueous Na₂CO₃ (Durst et al. 1988). Table 3.2 presents the starting materials and final products in the alkaline hydrolysis of GB.

The ΔH for the alkaline hydrolysis of GB is -44,400 cal/mol (Davis et al. 1977). An equilibrium constant of 10^{21.9} has been calculated from a ΔG of -30,000 cal/mol (Durst et al. 1988). GB is infinitely soluble in water. At 25°C and at pH 10, the half-life of GB is 5 minutes (Demek et al. 1970, cited in Rosenblatt et al. 1995). Yurow and Davis (1982) give a half-life of ~ 4 minutes for GB under the same conditions. They also report a half-life of <0.8 seconds for GB in 5% sodium hydroxide.

TABLE 3.2 Products of Alkaline Hydrolysis of GB

Principal Starting Materials	Principal Final Products
GB	Na[IMPA] NaF
Trace Starting Materials	Trace Final Products
Methylphosphonic difluoride	MPA F ⁻ (fluoride ion)
Diisopropyl methylphosphonate (DIMP)	DIMP (hydrolyzes slowly to IMPA)
N,N'-Diisopropylcarbodiimide	N,N'-Diisopropyl urea
Tributylamine	Tributylamine

Source: Rosenblatt et al. (1995).

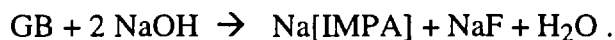
The term “toxic rebound” has been used to describe the re-formation of a small amount of GB when brine containing the hydrolyzed salts from alkaline hydrolysis of GB is spray dried. The more concentrated the salt solutions and the higher the acidity of the solution being spray dried, the higher the yield of GB will be. This re-formation phenomenon is of concern only when concentrations of the participating chemical species are high and heat is applied (Rosenblatt et al. 1995).

Beaudry and coworkers (1993) investigated the possibility of G agents re-forming in a 300-gallon neutralization tank that had been used for a series of chemical neutralization reactions. The G agents observed in that investigation finally were attributed to GB forming in the chloroform extract of acidified samples of the chemical neutralization solution. Re-formation of GB is not expected in dilute aqueous solution at high pH (Rosenblatt et al. 1995).

3.1.2 Chemical Neutralization of GB with Hypochlorite

GB is routinely neutralized with 5 to 7% aqueous NaOCl, 10% aqueous HTH, and aqueous STB slurry. This discussion applies to the chemical neutralization of GB in hypochlorite solution. The source of hypochlorite ion may be NaOCl, HTH, or STB. The role of hypochlorite ion in the chemical neutralization of GB is to provide hydroxide ion and to accelerate the reaction (Yurow and Davis 1982).

The chemical neutralization of GB in hypochlorite is an alkaline hydrolysis, with hypochlorite serving to accelerate the reaction. The reaction is described by the same equation that is used for alkaline hydrolysis:



The ^{31}P NMR evidence indicates that greater than 99.5% GB proceeds to greater than 99.5% Na[IMPA] in 5.25% NaOCl, with phosphorus-containing side products constituting less than 0.5% (Durst et al. 1988). Table 3.3 summarizes the starting materials and final products in the alkaline hydrolysis of GB in hypochlorite solution. The reaction is exothermic, but a value for the heat of reaction is not available. The reaction rate has been reported as “instantaneous” (Yurow and Davis 1982).

The information on the possibility of re-formation of GB from its alkaline hydrolysis products suggests that the re-formation of GB from the products resulting from reaction with hypochlorite is not likely.

3.1.3 Chemical Neutralization of GA by Alkaline Hydrolysis

GA has a solubility in water of 7.2% at 20°C (Field Manual 3-9). GA is routinely neutralized with 10 to 18% aqueous NaOH, 10% NaOH in alcohol, 8 to 10% aqueous Na_2CO_3 , and concentrated NH_4OH . This discussion applies specifically to the chemical neutralization of GA in 10% aqueous NaOH. It applies generally to three additional chemical neutralization

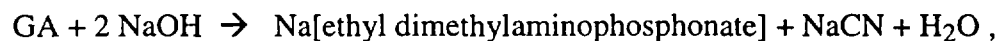
TABLE 3.3 Products of Alkaline Hydrolysis of GB in Sodium Hypochlorite Solution

Principal Starting Materials		Principal Final Products	
GB		Na[IMPA] NaF	
Trace Starting Materials		Trace Final Products	
Methylphosphonic difluoride		MPA	
		F^- (fluoride ion)	
DIMP		DIMP slowly hydrolyzes to IMPA	
N,N'-Diisopropylcarbodiimide		N,N'-Diisopropyl urea (possible reversible N,N'-chlorination of the urea, if hypochlorite is in high enough concentration)	
Tributylamine		Probably dibutylamine + butyraldehyde	
Hypochlorite (OCl^-)		Chlorate (ClO_3^-)	

Source: Rosenblatt et al. (1995).

procedures: GA in 10% NaOH in alcohol, GA in 10% aqueous Na₂CO₃, and GA in concentrated NH₄OH.

The chemical neutralization of GA in 10% aqueous sodium hydroxide proceeds by the following reaction:



where Na[ethyl dimethylaminophosphonate] is the sodium salt of ethyl dimethylaminophosphonic acid.

When sufficient quantities of GA are neutralized with aqueous hydroxide, it becomes necessary to destroy the cyanide ion that is produced to prevent formation of HCN if the solution is acidified. After neutralization is complete, treating the solution with hypochlorite converts the cyanide to nitrogen gas and carbonate ion (Yurow 1988).

The ³¹P NMR evidence indicates that greater than 99.5% GA proceeds to greater than 99.5% Na[ethyl dimethylaminophosphonate], with phosphorus-containing side products constituting less than 0.5%. Similar NMR results have been reported for the chemical neutralization of GA in 10% NaOH in alcohol and in 10% aqueous Na₂CO₃ (Durst et al. 1988). Table 3.4 presents the starting materials and final products in the alkaline hydrolysis of GA. The ΔH for the alkaline hydrolysis of GA at pH 9.5 and 25°C has been reported as -10,100 cal/mol. The half-life for that reaction was reported as 35 minutes (Yurow 1988). The half-life for the same reaction at pH 12 was reported to be 9.2 seconds (Durst et al. 1988).

On the basis of the discussion of the possibility of re-formation of GB from its alkaline hydrolysis products, the re-formation of GA from its alkaline hydrolysis products is not expected.

TABLE 3.4 Products of Hydrolysis of GA in Sodium Hydroxide

Principal Starting Materials	Principal Final Products
GA	Na[ethyl dimethylaminophosphonate], the sodium salt of ethyl dimethylaminophosphonic acid NaCN (sodium cyanide)
Trace Starting Materials	Trace Final Products
DIMP	DIMP very slowly hydrolyzes to IMPA

Sources: Yurow (1988); Rosenblatt et al. (1995).

3.1.4 Chemical Neutralization of GA with Hypochlorite

GA is routinely neutralized with 5 to 7% aqueous NaOCl, 10% aqueous HTH, and aqueous STB slurry. This discussion applies to the chemical neutralization of GA in hypochlorite solution. The source of hypochlorite ion may be NaOCl, HTH, or STB. The role of hypochlorite ion in the chemical neutralization of GA is to provide hydroxide ion and to accelerate the reaction.

According to Durst and coworkers (1988), when GA is neutralized with hypochlorite, both the cyano group and the dimethylamino group are lost, producing the ethyl ester of phosphonic acid. The other products of the reaction were not identified. The hypochlorite will react with the cyanide, converting it to nitrogen gas and carbonate ion (Yurow 1988).

The ^{31}P NMR evidence indicates that greater than 99.5% GA proceeds to greater than 99.5% Na[ethyl phosphonate], with phosphorus-containing side products constituting less than 0.5%. Table 3.5 presents the starting materials and final products in the alkaline hydrolysis of GA. The heat of reaction for the chemical neutralization of GA with hypochlorite has not been reported. It is expected to be exothermic by comparison with the alkaline hydrolysis of GA. Hypochlorite has been reported to catalyze the alkaline hydrolysis of GB and is expected to play a similar role in the reaction with GA (Yurow 1982).

Because the cyanide is converted irreversibly to nitrogen gas and carbonate ion, no re-formation of GA is expected after chemical neutralization with hypochlorite.

TABLE 3.5 Reaction of GA with Sodium Hypochlorite

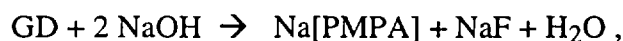
Principal Starting Materials	Principal Final Products
GA	Na[ethyl phosphonate], the sodium salt of ethyl phosphonic acid Possibly dimethylamine
Trace Starting Materials	Trace Final Products
DIMP OCI^-	DIMP slowly hydrolyzes to IMPA Chlorate (ClO_3^-)

Sources: Yurow (1988); Durst et al. (1988); Rosenblatt et al. (1995).

3.1.5 Chemical Neutralization of GD by Alkaline Hydrolysis

GD has a solubility of 2.1% in water at 20°C (Field Manual 3-9). Like the other G agents, it is susceptible to alkaline hydrolysis. Because of the low solubility of GD in water, addition of an alcohol can increase solubility and therefore the overall rate of chemical neutralization (Rosenblatt et al. 1995). Dugway Proving Ground routinely neutralizes GD with 10% NaOH in alcohol (10% NaOH in a mixture of 80/20 denatured ethanol and water) and with concentrated NH_4OH . This discussion applies specifically to the chemical neutralization of GD in 10% NaOH in alcohol and generally to the chemical neutralization of GD in concentrated NH_4OH .

The chemical neutralization of GD in alcoholic sodium hydroxide proceeds by the following reaction:



where Na[PMPPA] is the sodium salt of pinacolyl methylphosphonic acid.

The ^{31}P NMR evidence indicates that greater than 99.5% GD proceeds to greater than 99.5% Na[PMPPA], with phosphorus-containing side products constituting less than 0.5% for the chemical neutralization of GD in 10% NaOH in alcohol. Similar results were found for the neutralization of GD in 10% aqueous NaOH and in 10% aqueous Na_2CO_3 (Durst et al. 1988).

The presence of alcohol in solution does not significantly inhibit the reactivity of GD or the other G agents with hydroxide ion. A solution of hydroxide in methanol forms methoxide ion. The methoxide ion reacts as a nucleophile to attack the central phosphorus atom to form the ester, methyl pinacolyl methylphosphonate. This ester eventually undergoes hydrolysis to form PMPPA and perhaps some methyl methylphosphonic acid (Rosenblatt et al. 1995). A set of parallel reactions may occur with GD in ethanol solution. Table 3.6 presents the starting materials and final products in the alkaline hydrolysis of GD.

The half-life of GD in excess 5% aqueous sodium hydroxide is 0.08 hour at 20°C. The heat of reaction is estimated to be similar to that of GB (-44,400 cal/mole) because fluorine is the leaving group in both cases (Yurow 1988).

Re-formation of GB is not expected in dilute aqueous solution at high pH (Rosenblatt et al. 1995), so re-formation of GD is not expected under the same conditions because of their similar structures and reaction mechanisms.

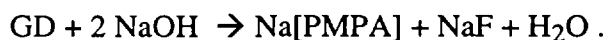
TABLE 3.6 Products of Alkaline Hydrolysis of GD

Principal Starting Materials	Principal Final Products
GD	Na[PMPA] NaF (sodium fluoride)
Trace Starting Materials	Trace Final Products
Methylphosphonic difluoride	MPA F ⁻
DIMP	DIMP slowly hydrolyzes to IMPA
Possible side reaction with ethoxide ion	Possibly ethyl pinacolyl methylphosphonate hydrolyzing to Na[pinacolyl methylphosphonate] and Na[ethyl methylphosphonate]

Sources: Durst et al. (1988); Rosenblatt et al. (1995).

3.1.6 Chemical Neutralization of GD with Hypochlorite

Dugway Proving Ground routinely neutralizes GD with 5% aqueous NaOCl, 10% aqueous HTH, and aqueous STB slurry. This discussion applies to the chemical neutralization of GD in hypochlorite solution. The source of hypochlorite ion may be NaOCl, HTH, or STB. The chemical neutralization of GD in hypochlorite is an alkaline hydrolysis. The role of hypochlorite ion in the neutralization of GD is to provide hydroxide ion and to accelerate the reaction (Yurow 1988). The reaction is described by the same equation used for alkaline hydrolysis:



The ³¹P NMR evidence indicates that greater than 99.5% GD proceeds to greater than 99.5% Na[PMPA], with phosphorus-containing side products constituting less than 0.5% for the chemical neutralization of GD in 5.25% NaOCl (Durst et al. 1988). Table 3.7 presents the starting materials and final products in the alkaline hydrolysis of GB in 5.25% NaOCl solution.

The reaction is expected to be exothermic. The use of an alcohol in the chemical neutralization solution is expected to increase the overall rate of neutralization by enhancing the solubility of GD. By comparison with GB, the reaction rate is expected to be faster than that of the corresponding alkaline hydrolysis reaction in the same solvent because of the catalytic effect of hypochlorite ion upon alkaline hydrolysis.

TABLE 3.7 Products of Alkaline Hydrolysis of GD in Sodium Hypochlorite Solution

Principal Starting Materials	Principal Final Products
GD	Na[PMPA] (sodium salt PMPA) NaF
Trace Starting Materials	Trace Final Products
Methylphosphonic difluoride	MPA F ⁻
DIMP OCl ⁻	DIMP slowly hydrolyzes to IMPA ClO ₃ ⁻

Sources: Durst et al. (1988); Rosenblatt et al. (1995).

On the basis of the discussion of the possibility of re-formation of GB from its alkaline hydrolysis products, the re-formation of GD from the products resulting from reaction with hypochlorite solution is not expected.

3.1.7 Chemical Neutralization of TGD

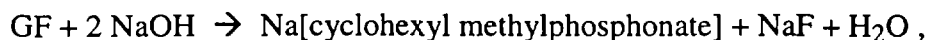
TGD is GD thickened with a polymer. Little specific information was found regarding the chemical neutralization of TGD (thickened GD) or other thickened agents. UCON 75-H-90,000 is a polyethylene glycol derivative that has been used to thicken GB, a related G agent. Thickeners are added to GD to increase persistence in the field. In general, thickened agents form large droplets that provide for a greater concentration reaching the ground and a greater contact hazard than the unthickened forms (Field Manual 3-9).

Yang and coworkers (1992) have noted that an organic solvent often is added to an aqueous neutralization solution to improve solubility of thickened agents. The actual neutralization reaction remains the same for the thickened agent after it is in solution. However, many of the oxidation and substitution reactions become slower as the solvent polarity decreases. The chemical neutralization solution recommended for TGD is 10% NaOH in alcohol.

3.1.8 Chemical Neutralization of GF by Alkaline Hydrolysis

GF is the least soluble of the G agents considered in this report. It has a solubility of 0.37% in water at 20°C (Field Manual 3-9). Like the other G agents, it is subject to alkaline hydrolysis. Dugway Proving Ground routinely neutralizes GF with 10% aqueous NaOH, 10% NaOH in alcohol, 10% aqueous Na₂CO₃, and concentrated NH₄OH.

Little information concerning the alkaline hydrolysis of GF was found. However, because of similarities in structure to GB and GD, GF is expected to hydrolyze rapidly in alkaline solution according to the following reaction:



where Na[cyclohexyl methylphosphonate] is the sodium salt of cyclohexyl methylphosphonic acid.

The relative insolubility of GF is expected to lower the overall rate of neutralization. The solution of 10% NaOH in alcohol is expected to be the most effective of the chemical neutralization solutions recommended for use at Dugway Proving Ground. Table 3.8 presents the starting materials and final products in the alkaline hydrolysis of GF on the basis of comparison with GB and GD.

By comparison with GB and GD, the reaction with GF is expected to be exothermic, and at pH 12 its half-life is expected to be in the range of the half-lives of GB (3 seconds) and GD (7 seconds). It may be necessary to use alcohol to dissolve GF into the neutralization solution.

Re-formation of GB is not expected in dilute aqueous solution at high pH (Rosenblatt et al. 1995), and because of their similar structures and reaction mechanisms, re-formation of GF is not expected under the same conditions.

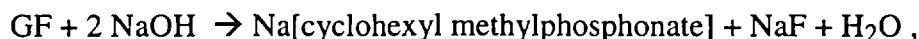
3.1.9 Chemical Neutralization of GF with Hypochlorite

Dugway Proving Ground routinely neutralizes GF with 5% aqueous NaOCl, 10% aqueous HTH, and aqueous STB slurry. This discussion applies to the chemical neutralization of GF in hypochlorite solution in general. The source of hypochlorite ion may be NaOCl, HTH, or

TABLE 3.8 Products of Alkaline Hydrolysis of GF

Principal Starting Materials	Principal Final Products
GF	Na[cyclohexyl methylphosphonate] (sodium salt of cyclohexyl methylphosphonic acid) NaF
Trace Starting Materials	Trace Final Products
DIMP	DIMP slowly hydrolyzes to IMPA

STB. Little information concerning the reaction of GF with hypochlorite was found. On the basis of similarities in structure to GB and GD, it is expected to undergo rapid hydrolysis. The role of hypochlorite ion in the chemical neutralization of GF is to provide hydroxide ion and to accelerate the reaction (Yurow 1988). The reaction would be described by the same equation that is used for alkaline hydrolysis:



where Na[cyclohexyl methylphosphonate] is the sodium salt of cyclohexyl methylphosphonic acid.

Table 3.9 presents the starting materials and final products expected for the alkaline hydrolysis of GF in 5.25% NaOCl solution on the basis of comparison with GB and GD.

The reaction is expected to be exothermic. The reaction rate is expected to be similar to that of the alkaline hydrolysis reaction, recognizing the effect of limited solubility and the catalytic effect of hypochlorite ion upon alkaline hydrolysis.

On the basis of the discussion of the possibility of re-formation of GB from its alkaline hydrolysis products, re-formation of GF from the products resulting from reaction with hypochlorite solution is not expected.

TABLE 3.9 Products of Alkaline Hydrolysis of GF in Sodium Hypochlorite Solution

Principal Starting Materials	Principal Final Products
GF	Na[cyclohexyl methylphosphonate] (sodium salt of cyclohexyl methylphosphonic acid) NaF
Trace Starting Materials	Trace Final Products
DIMP OCl ⁻	DIMP slowly hydrolyzes to IMPA ClO ₃ ⁻

3.1.10 Chemical Neutralization of VX by Alkaline Hydrolysis

VX is only slightly soluble in water at room temperature. Below 9.4°C it is miscible with water (Field Manual 3-9). VX is routinely neutralized with 10 to 18% aqueous NaOH and 10% NaOH in alcohol.

The hydrolysis of VX proceeds by multiple pathways and results in a more complex set of products than the hydrolysis of the G agents. Across the pH range, the P–S bond is cleaved to give two primary products: EMPA and DESH. EA 4196 is formed by air oxidation of DESH and is believed to be a powerful vesicant, similar in effect to mustard (Small 1983, cited in Rosenblatt et al. 1995). In the middle and higher pH ranges, additional reaction pathways contribute to the mix of hydrolysis products. In addition to P–S bond cleavage, the P–O–C bond to the ethoxy group and the C–S bond also are broken (Epstein et al. 1974, cited in Rosenblatt et al. 1995). The product of ethoxy group cleavage, EA 2192, is comparatively stable towards hydrolysis. Contrary to earlier opinion, Yang and coworkers (1992) demonstrated that up to 13% EA 2192 formed during the hydrolysis of VX even in aqueous 0.1 M NaOH. Szfraniec and coworkers (1993, cited in Rosenblatt et al. 1995), who found that 17% EA 2192 formed in aqueous 2.0 M NaOH, confirmed this. The C–S bond cleavage in the neutral pH range results in the formation of O-ethyl methylphosphonothioic acid, diisopropylaminoethyl sulfide, and possibly other minor products (Epstein et al. 1974, Yang et al. 1990, cited in Rosenblatt et al. 1995).

The ^{31}P NMR evidence confirms that in alcoholic NaOH, VX reacts to form the sodium salts of EMPA and EA 2192 (Durst et al. 1988). Table 3.10 summarizes the starting materials and final products in the alkaline hydrolysis of VX.

A heat of reaction for the alkaline hydrolysis of VX was not found. VX hydrolysis rates are slower than those of the G agents. A half-life of 2.5 hours has been reported for the hydrolysis of VX in water at pH 12 at 25°C (Epstein et al. 1974, cited in Rosenblatt et al. 1995).

According to Rosenblatt et al. (1995), it is extremely unlikely that VX, once hydrolyzed, would form again under any conditions.

3.1.11 Chemical Neutralization of VX with Hypochlorite in Basic Solution

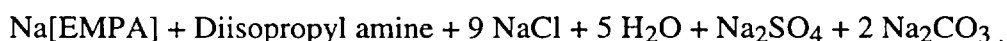
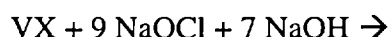
VX is routinely neutralized with 5 to 7% aqueous NaOCl, 10% aqueous HTH, and aqueous STB slurry. This discussion applies to the neutralization of VX in hypochlorite solution at a high pH. The source of hypochlorite ion may be NaOCl, HTH, or STB. The reactions of

TABLE 3.10 Products of Alkaline Hydrolysis of VX

Principal Starting Materials	Principal Final Products
VX	Na[EMPA] (sodium salt of ethyl methylphosphonic acid) DESH (2-diisopropylaminoethanethiol) EA 2192
	Product of Air Oxidation
	EA 4196 [Bis(2-diisopropylaminoethyl) disulfide] formed by the air oxidation of DESH
	Products Formed Closer to Neutral pH
	O-ethyl methylphosphonothioic acid Diisopropylaminoethyl sulfide
Trace Starting Materials	Trace Final Products
N,N'-diisopropylcarbodiimide	N,N'-diisopropylurea
N,N'-dicyclohexylcarbodiimide	N,N'-dicyclohexylurea

Source: Rosenblatt et al. (1995).

hypochlorite with VX in basic solution have not been completely defined. With sufficient excess hypochlorite, the stoichiometry of the reaction has been reported as:



where Na[EMPA] is the sodium salt of EMPA (Durst et al. 1988).

The ^{31}P NMR evidence indicates that VX forms the anion of EMPA plus a small amount of the anion of methylphosphonic acid in 5.25% NaOCl (Durst et al. 1988). Table 3.11 presents the starting materials and final products in the alkaline hydrolysis of VX in basic hypochlorite solution. The reaction is exothermic, with a heat of reaction reported at "approximately -700,000 cal/mol" for the reaction of VX with alkaline hypochlorite. The reaction rate in 10% HTH has been reported as ~ 70 seconds at 25°C (Yurov and Davis 1982).

TABLE 3.11 Products of Neutralization of VX in Sodium Hypochlorite Solution

Principal Starting Materials	Principal Final Products
VX [O-ethyl S-(2-diisopropylaminoethyl) methylphosphonothioate]	Na[EMPA] (sodium salt of ethyl methylphosphonic acid) Sulfate, carbonate, chloride, and diisopropyl amine
Trace Starting Materials	Trace Final Products
N,N'-diisopropylcarbodiimide N,N'-dicyclohexylcarbodiimide	N,N'-diisopropylurea (possibly reversibly chlorinated) N,N'-dicyclohexylurea (possibly reversibly chlorinated) Na[methylphosphonate]
OCI ⁻	Chlorate (ClO ₃ ⁻)

Sources: Rosenblatt et al. (1995); Durst et al. (1988).

With the formation of sulfate, carbonate, and diisopropylamine during the reaction of VX with hypochlorite, the chemical agent is completely disrupted and it is extremely unlikely that VX would form again under any conditions (Rosenblatt et al. 1995).

3.1.12 Chemical Neutralization of Vx by Alkaline Hydrolysis

Vx is only slightly soluble in water at room temperature (Field Manual 3-9). Dugway Proving Ground neutralizes Vx with 10% aqueous NaOH, 10% NaOH in alcohol, 10% aqueous Na₂CO₃, and concentrated NH₄OH.

The hydrolysis of Vx is expected to proceed similarly to that of VX. Table 3.12 summarizes the presumed starting materials and final products in the alkaline hydrolysis of Vx. It is possible that Vx would require the addition of a stabilizer for long-term storage. It is not known whether a stabilizer was used with stored Vx.

By comparison with VX, it is extremely unlikely that Vx, once hydrolyzed, would form again under any conditions.

3.1.13 Chemical Neutralization of Vx with Hypochlorite in Basic Solution

Dugway Proving Ground neutralizes Vx with 5% aqueous NaOCl, 10% aqueous HTH, and aqueous STB slurry. This discussion applies to the decontamination of Vx in hypochlorite solution at a high pH; the source of hypochlorite ion may be NaOCl, HTH, or STB.

The reactions of hypochlorite with Vx in basic solution are expected to be similar to those with VX. Table 3.13 summarizes the products of decontamination of Vx in NaOCl. By comparison with the reaction of VX, the reaction of Vx with hypochlorite probably is rapid and exothermic. With the formation of sulfate, carbonate, and dimethylamine during the reaction of Vx with hypochlorite, the chemical agent is completely disrupted, and it is extremely unlikely that Vx would form again under any conditions.

TABLE 3.12 Products of Alkaline Hydrolysis of Vx

Principal Starting Materials	Principal Final Products
Vx	Na[iBMPA] (sodium salt of iso-butyl methylphosphonic acid) 2-Ethylaminoethanethiol Vx analog of EA 2192
	Product of Air Oxidation
	Vx analog of EA 4196 formed by the air oxidation of 2-ethylaminoethanethiol
	Products Formed Closer to Neutral pH
	O-isobutyl methylphosphonothioic acid Diethylaminoethyl sulfide
Trace Starting Materials	Trace Final Products
N,N'-diisopropylcarbodiimide	N,N'-diisopropylurea
N,N'-dicyclohexylcarbodiimide	N,N'-dicyclohexylurea

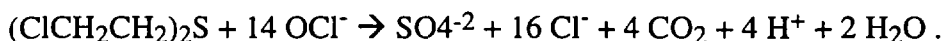
TABLE 3.13 Products of Neutralization of Vx in Sodium Hypochlorite Solution

Principal Starting Materials	Principal Final Products
Vx	Na[iBMPA] (sodium salt of iso-butyl methylphosphonic acid) Sulfate, carbonate, chloride, and dimethyl amine
Trace Starting Materials	Trace Final Products
N,N'-diisopropylcarbodiimide	N,N'-diisopropylurea (possibly reversibly chlorinated)
N,N'-dicyclohexylcarbodiimide	N,N'-dicyclohexylurea (possibly reversibly chlorinated)
OCl ⁻	Chlorate (ClO ₃ ⁻)

3.1.14 Chemical Neutralization of H/HD with Hypochlorite in Basic Solution

HD is less than 1% soluble in water (Field Manual 3-9). H/HD is routinely neutralized with 5 to 7% aqueous NaOCl, 10% aqueous HTH, and aqueous STB slurry. This discussion applies to the chemical neutralization of H/HD in hypochlorite solution at a high pH; the source of hypochlorite ion may be NaOCl, HTH, or STB.

Under optimum conditions (excess neutralization reagent, high pH, and adequate stirring) hypochlorite will oxidize H/HD to sulfate, chloride, and carbon dioxide according to the following equation:



The ^{13}C NMR analysis of one such reaction mixture revealed greater than 99.5% destruction of HD and the formation of about 20 uncharacterized carbon-containing products. With a deficiency of hypochlorite, the sulfoxide and/or the sulfone of mustard may persist (Durst et al. 1988).

Little is known about the effect of hypochlorite upon the impurities produced during the manufacture of mustard. It is likely that conditions favorable to the complete mineralization of mustard to sulfate, chloride, and carbon dioxide will also oxidize the additional sulfur atoms in the polysulfides. Other sulfur-containing impurities probably would be oxidized as well (if not to sulfate, at least to sulfoxides, sulfones, or sulfonic acids) (Rosenblatt et al. 1995). Table 3.14 lists the starting materials and final products in the alkaline hydrolysis of H/HD in basic hypochlorite solution.

Yurow and Davis (1982) characterize the reaction of mustard with hypochlorite as "highly exothermic." Half-life data for the reaction were not found in this research. With the formation of sulfate, chloride, and carbon dioxide during the reaction of HD with hypochlorite, there is no reason to expect re-formation of HD (Rosenblatt et al. 1995).

3.1.15 Chemical Neutralization of HT with Hypochlorite in Basic Solution

The HT mixture is barely soluble in water (Field Manual 3-9). HT is routinely neutralized with 5 to 7% aqueous NaOCl, 10% aqueous HTH, and aqueous STB slurry at a high pH. This discussion applies to the chemical neutralization of HT in hypochlorite solution. The source of hypochlorite ion may be NaOCl, HTH, or STB.

Agent T has not been studied as a separate agent. Its chemistry is very close to that of mustard, and the neutralization reactions of mustard are expected to apply to HT with small

TABLE 3.14 Products of Neutralization of H/HD in Sodium Hypochlorite Solution

[illegible]

Source: Rosenblatt et al. (1995).

differences attributable to solubility and reaction rates (Durst et al. 1988). Therefore, under optimum conditions (excess neutralization reagent, high pH, and adequate stirring), hypochlorite is expected to oxidize HT as well as mustard to sulfate, chloride, and carbon dioxide (Durst et al. 1988).

3.1.16 Chemical Neutralization of HQ with Hypochlorite in Basic Solution

The HQ mixture is expected to behave similarly to the HT mixture. Because Dugway Proving Ground neutralizes HT with 5% aqueous NaOCl, 10% aqueous HTH, and aqueous STB slurry at a high pH, these chemical neutralization solutions are expected to perform similarly for HQ.

Q has not been studied as a separate agent. Its chemistry is very close to that of mustard, and the chemical neutralization reactions of mustard are expected to apply to HQ, with small differences attributable to solubility and reaction rates. Therefore, under optimum conditions (excess neutralization reagent, high pH, and adequate stirring), hypochlorite is expected to oxidize HQ as well as mustard to sulfate, chloride, and carbon dioxide.

3.1.17 Chemical Neutralization of HN1 and HN3 with Hypochlorite in Basic Solution

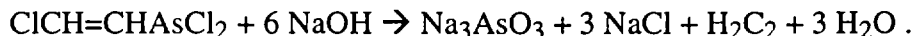
HN1 and HN3 are sparingly soluble in water, with HN3 being the least soluble (Field Manual 3-9). Dugway Proving Ground neutralizes HN1 and HN3 with 5% aqueous NaOCl, 10% aqueous HTH, and aqueous STB slurry. Yurow and Davis (1982) reported that the only information found concerning aqueous oxidative neutralization of the nitrogen mustards was a reference to some exploratory studies.

3.1.18 Chemical Neutralization of L with Hypochlorite in Basic Solution

L is insoluble in water (Field Manual 3-9). L is routinely neutralized with 5 to 7% aqueous NaOCl, 10% aqueous HTH, and aqueous STB slurry at a high pH. This discussion applies to the chemical neutralization of L in hypochlorite solution; the source of hypochlorite ion may be NaOCl, HTH, or STB.

Four substances have been found in stored L. L1 is the primary component. L2 is also a vesicant and may be present up to 10% or 20%; some AsCl_3 is present as well (Yurow and Davis 1982). L3 is found in stored L. Smith and coworkers (1993) reported the analysis of a sample of distilled L. They found 95% trans isomer, <2% cis isomer, and 3% of a geminal isomer that has the chlorine attached to the carbon atom bonded to arsenic. The presence of the geminal isomer may explain Hewitt's report (1948) that an isomer of L dissolved in cold NaOH without the evolution of acetylene and formed vinyl chloride when the solution was warmed to 40°C.

Most of the information discovered regarding the chemical neutralization of L focuses upon alkaline hydrolysis, which limits the formation of lewisite oxide, ClCH=CHAsO . When mixed with water, L forms lewisite oxide, which goes on to polymerize. Lewisite oxide can slowly hydrolyze to 2-chlorovinylarsonous acid (CVAA) in aqueous media. While CVAA is only minimally soluble in water, it may be present in typically caustic decontamination solution. The alkaline hydrolysis is written as (Yurow and Davis 1982):



The formation of acetylene is temperature and pH dependent. Waters and Williams (1950) reported that to form acetylene, the pH of a solution of L must be at least 10.5 at 16°C and at least 9 at 50°C.

Durst and coworkers (1988) cited a report by Buswell and Price (1944) that the reaction of L with hypochlorite has been studied, but because of the relatively slow kinetics of oxidation in solution, it offers no advantage over aqueous sodium hydroxide. According to Durst and coworkers (1988), the reaction of L with 5.25% NaOCl in aqueous solution proceeds as an alkaline hydrolysis, producing arsenite, chloride, and acetylene, with the hypochlorite serving as

a source of hydroxide. The ^{13}C NMR spectra confirm the rapid disappearance of L from the solution. Small traces of some uncharacterized carbon compounds remained. Evidently not much L2 was present in the NMR sample. The evolution of acetylene was observed (Durst et al. 1988). The hypochlorite will oxidize the arsenite (AsO_3^{-3}) to arsenate (AsO_4^{-3}).

Table 3.15 lists the starting materials and final products in the chemical neutralization of L in basic hypochlorite solution. The alkaline hydrolysis reaction has been reported as complete in less than 10 seconds with a heat of reaction of -102,000 cal/mol. L2 appears to decompose more slowly in aqueous sodium hydroxide than does lewisite (Yurow and Davis 1982).

With the formation of acetylene during the reaction of L with hypochlorite, there is no reason to expect the re-formation of L.

TABLE 3.15 Products of Neutralization of L in Sodium Hypochlorite Solution

Principal Starting Material	Principal Final Products
L or L1	Acetylene, AsO_3^{-3} , and chloride ion
Other Starting Materials	Other Final Products
L2 and L3	Probably acetylene, AsO_3^{-3} , and chloride ion
Geminal-lewisite, $(\text{CH}_2=\text{CHClAsCl}_2)$	Vinyl chloride, and possibly AsO_4 , and chloride ion
AsCl_3	AsO_3^{-3}
OCl^-	ClO_3^-

Sources: Yurow and Davis (1982); Durst et al. (1988); Smith et al. (1998).

3.1.19 Chemical Neutralization of HL with Hypochlorite in Basic Solution

HL is a variable combination of HD and L that provides a mixture of low freezing point for use in cold weather operations or in high-altitude spray (Field Manual 3-9). Because H and L are not very soluble in water, the mixture is not expected to be soluble in water either. Dugway Proving Ground neutralizes HL with 5% aqueous NaOCl , 10% aqueous HTH, and aqueous STB slurry.

Little information was found regarding the chemical neutralization of HL mixtures specifically. Yurow and Davis (1982) recommended the use of 2-aminoethanol as a neutralization solution for HL. The chemical neutralization reactions of mustard and L in hypochlorite are expected to apply to HL.

3.1.20 Applicability of Chemical Neutralization as a Treatment Technology for Chemical Agent Related Waste Streams

The identification of neutralization products for chemical agents discussed above is based on results from experiments performed in solution rather than chemical agent related waste streams (K901-K908). The waste streams include solid materials that have been exposed to chemical agents. The exposure of impermeable, chemically unreactive substrates (such as stainless steel or glass) to chemical agents will result in minimal sorption of the agents. Painted metal is expected to absorb more, while plastics and elastomers would absorb even more. The chemical neutralization solutions used do not penetrate permeable materials (paint, plastics, and elastomers), and additional time is required for the chemical agent to diffuse out of the permeable material into the chemical neutralization solution. Once the chemical agent diffuses out of the permeable material into the neutralization solution, its neutralization rate follows solution neutralization rates. The amount of agent absorbed by permeable substrates is a function of the concentration of agent and the time of exposure. The longer the delay between exposure of a permeable substrate to agent and the application of neutralization solution, the longer the chemical neutralization process is expected to take (Rosenblatt et al. 1995).

Some chemical agent related waste streams may also contain water-immiscible solvents, such as chloroform or heptane. These solvents accumulate when standard solutions of agents or solutions of agent extracted from solid test items are discarded. In some situations, separate layers form in the chemical neutralization vessel. Representative samples of the contents of liquid waste drums are collected for agent analysis before disposal.

3.2 PERFORMANCE DATABASE

This section presents the performance database. Chemical neutralization procedures used will be considered demonstrated if the data presented in the database indicate that the chemical agent concentration is equal to or below the proposed LDR concentration standards identified for the chemical agents. The sample descriptions provided in the Dugway Proving Ground database were taken directly from the description provided with the analytical sample. The samples in the DCD, CAMDS, and TOCDF databases are primarily brines from the chemical neutralization of liquid and solid laboratory wastes, but also include some analysis of sump liquids and brine from the neutralization of solid wastes. DCD and CAMDS generally use the alkaline hydrolysis reaction for GB neutralization and the alkaline hypochlorite reaction for VX and H neutralization. To date, TOCDF has only neutralized GB with the alkaline hydrolysis reaction. Databases from DPG, DCD, CAMDS, and TOCF are shown in Tables 3.16 through 3.19, respectively.

TABLE 3.16 DPG Performance Database^{a,b}

Sample Description	Chemical Laboratory Number	Chemical Laboratory Analysis Date	Reported Chemical Agent Concentration							
			GA	GB	GD	GF	HD	HN3	VX	L
HTH/soda ash decontamination	97-050, DUP	3/27/97	-	ND	-	-	-	-	-	-
Soda ash/nitric acid decontamination	97-063-1	4/8/97	-	ND	-	-	-	-	-	-
Water and soda ash, bleaches/rinses from chemical decontamination	97-063-2	4/8/97	-	ND	-	-	-	-	-	-
HTH/nitric acid decontamination	97-063-3	4/8/97	-	ND	-	-	-	-	-	-
Waste, alcoholic caustic decontamination	97-068-1, 2	4/22/97, 4/29/97	-	-	ND	-	ND	-	ND	-
L bleach decontamination	97-080, DUP	5/16/97	-	-	-	-	-	-	-	ND
Bleach decontamination	97-081, DUP	5/15/97	-	ND	-	-	ND	-	-	-
Bleach decontamination	97-082	5/15/97, 5/16/97	-	-	ND	-	ND	-	ND	-
Bleach decontamination solutions	97-099, DUP	6/10/97, 6/24/97	ND	ND	ND	ND	ND	-	ND	-
Alcohol/caustic decontamination solutions	97-100, DUP	6/10/97, 6/24/97	ND	ND	ND	ND	ND	-	ND	-
Technicon nerve agent analysis waste, caustics/alcohols from chemical decontamination, liquid decontamination, analysis of VX waste, may contain water, acetate buffers, enzymes	97-110 A, B	7/19/97	-	-	-	-	-	-	ND	-
Spent bleach decontamination solutions, agent decontamination and rinses, may contain water, HTH, chloroform	97-111 A, B	7/16/97, 7/19/97	ND	ND	ND	ND	ND	-	ND	-
Water, bleach rinses, decontamination agent bleach waste GD, HD, VX	97-112 A, B	7/16/97	-	-	ND	-	ND	-	ND	-
Water, bleach decontamination rinses (STB)	97-112 A, B	7/16/97	-	-	ND	-	ND	-	ND	-
Bleach waste, Technicon liquid, from Technicon enzymatic analysis	97-113 A, B	7/19/97	-	-	-	-	-	-	ND	-
Bleach decontamination waste, liquid decontamination of VX waste, composite of 10 drums, may contain water, VX, HTH	97-113 C, D	7/19/97	-	-	-	-	-	-	ND	-
Waste, alcohol caustics solutions, alcohol caustic decontamination solutions, may contain water, acetone, isopropyl alcohol	97-120 A, B	8/5/97, 8/6/97	-	ND	-	-	ND	-	ND	-

TABLE 3.16 (Cont.)

Sample Description	Chemical Laboratory Number	Chemical Laboratory Analysis Date	Reported Chemical Agent Concentration							
			GA	GB	GD	GF	HD	HN3	VX	L
Waste bleach decontamination solutions, may contain water, HTH	97-121 A, B	8/5/97, 8/6/97	ND	ND	ND	ND	ND	-	ND	-
Waste alcohol/caustic, liquid caustic decontamination solutions, caustic alcohols for decontamination of GB, GF, may contain isopropyl alcohol, water, sodium hydroxide	97-130 A, B	8/25/97	-	ND	-	ND	-	-	-	-
Alcohol/caustic decontamination solution, liquid, alcohol caustic decontamination solution of GB, GF, may contain isopropyl alcohol, ethanol, water	97-131 A, B	8/25/97	-	ND	-	ND	-	-	-	-
Alcohol/caustic waste decontamination solution, caustic liquid decontamination solution, agent decontamination with caustic solutions	97-138 A, B	9/15/97, 9/17/97	ND	ND	ND	ND	ND	-	ND	-
Waste, lewisite bleach decontamination solution, liquid	97-139 A, B	9/11/97	-	-	-	-	-	-	-	ND
Liquid bleach decontamination solution, agent decontamination with bleach solutions	97-140 A, B	9/15/97, 9/17/97	ND	ND	ND	ND	ND	-	ND	-
Bleach decontamination solution, water, solids: PPE, glass, chem-wipes	97-147 A, B	9/25/97, 9/29/97	ND	ND	ND	ND	ND	-	ND	-
Alcohol/caustic solid/liquid decontamination: PPE, glassware, chem-wipes, plastic bags, alcohol/caustic decontamination of solids and liquids	97-153 A, B	10/20/97	ND	ND	ND	ND	ND	-	ND	-
Liquid bleach decontamination of L, may contain calcium, hypochlorite, water L decontamination	97-156 A, B	10/20/97	ND	ND	ND	ND	ND	-	ND	ND
Bleach decontamination of solid/liquid combination	97-161 A, B	10/29/97, 10/30/97	ND	ND	ND	ND	ND	-	ND	-
Liquid bleach decontamination of L, from decontamination of hoses, the history of which showed all agents including L, may contain bleach, water, traces of alcohol	97-162 A, B	11/29/97, 11/30/97	ND	ND	ND	ND	ND	-	ND	ND
Liquid bleach decontamination, solid/liquid combination waste, decontamination with bleaches of agents which are test generated	97-167 A, B	11/4/97, 11/6/97	ND	ND	ND	-	ND	-	ND	-

TABLE 3.16 (Cont.)

Sample Description	Chemical Laboratory Number	Chemical Laboratory Analysis Date	Reported Chemical Agent Concentration							
			GA	GB	GD	GF	HD	HN3	VX	L
DP55, liquid/solid, decontamination of solids and liquids exposed to agents through testing, solids and liquids in alcohol/caustic decontamination solutions	97-175 A, B	12/8-11/97	ND	ND	ND	ND	ND	-	ND	-
Liquid/solid, decontamination of agents and solid items with bleaches	97-178 A, B	12/8-11/97	ND	ND	ND	ND	ND	-	ND	-
Solid/liquid combination, alcohol/caustics, generated through the decontamination with caustics process	98-004 A, B	1/29/98	ND	ND	ND	ND	ND	-	ND	-
Bleach decontamination of solid/liquid combination waste, generated through lab cleanup	98-011 A, B	2/4/98	ND	ND	ND	ND	ND	-	ND	ND
Bleach decontamination process waste, solid/liquid from multiple tests	98-012A, B	2/4/98	ND	ND	ND	ND	ND	-	ND	-

^a Notation:

- = not analyzed
 ND = not detected.

^b Detection limits are based on chemical agent in brine and are as follows:

GA, 0.02 milligrams/liter (mg/L)
 GB, 0.02 mg/L
 GD, 0.02 mg/L
 GF, 0.02 mg/L
 VX, 0.02 mg/L
 HD, 0.2 mg/L
 L, 2.0 mg/L.

TABLE 3.17 DCD Performance Database^{a,b}

Chemical Laboratory Number	Chemical Laboratory Analysis Date	Reported Chemical Agent Concentration		
		GB	VX	H
SAF 2102	2/98	ND	-	-
SAF 2105	2/98	ND	-	-
SAF 2114	2/98	-		ND
SAF 2122	2/98	-	ND	-
SAF 2125	2/98	-	-	ND
SAF 2115	3/98	-	-	ND
SAF 2107	4/98	-	-	ND
SAF 2112	4/98	ND	-	-
SAF 2126	4/98	ND	-	-
SAF 2127	4/98	ND	-	-
1483	4/97	ND	ND	ND
1484	4/97	ND	ND	ND
1485	4/97	ND	ND	ND
1486	4/97	ND	ND	ND
1487	4/97	-	-	ND
1488	4/97	ND	-	-
1489	4/97	ND	-	-
1490	4/97	ND	-	-
1491	4/97	ND	-	-
1492	4/97	ND	-	-
1493	4/97	-	ND	ND
1494	4/97	ND	ND	ND
SAF 1482	4/97	ND	ND	ND
SAF 1496	4/97	ND	ND	ND
SAF 735	3/96	ND	-	
SAF 836	5/96	ND	-	
SAF 837	5/96	ND	-	
SAF 841	5/96	ND	-	
SAF 907	7/96		-	ND
SAF 908	7/96		-	ND
SAF 910	7/96	ND	-	
SAF 911	7/96	ND	-	

TABLE 3.17 (Cont.)

Chemical Laboratory Number	Chemical Laboratory Analysis Date	Reported Chemical Agent Concentration		
		GB	VX	H
SAF 912	7/96	–	ND	–
SAF 913	7/96	–	ND	–
SAF 914	7/96	ND	ND	–
SAF 960	7/96	ND	–	–
SAF 964	8/96	ND	–	–
SAF 158	6/95	–	–	ND
SAF 218	8/95	ND	–	ND
SAF 220	8/95	–	–	ND
SAF 243	10/95	ND	–	–
541-8223	3/94	–	–	ND
541-8227	3/94	–	ND	–
541-5360	8/94	–	ND	–
541-8003	8/94	ND	–	–
541-8444	10/94	ND	–	–
541-8446	10/94	ND	–	–
541-8536	12/94	ND	ND	–
541-4847	2/93	–	–	ND
SAF 3248	5/93	–	ND	–
SAF 3249	5/93	ND	ND	–
SAF 159	6/93	ND	–	–
541-7028	7/93	–	–	ND
SAF 3248	8/93	ND	–	–
99-93-119	8/93	ND	–	–
99-93-120	8/93	ND	–	–
99-93-121	8/93	ND	–	–
99-93-122	8/93	ND	–	–
99-93-123	8/93	ND	–	–
99-93-124	8/93	ND	–	–
99-93-125	8/93	ND	–	–
99-93-126	8/93	ND	–	–
99-93-127	8/93	ND	–	–
99-93-128	8/93	ND	–	–

TABLE 3.17 (Cont.)

Chemical Laboratory Number	Chemical Laboratory Analysis Date	Reported Chemical Agent Concentration		
		GB	VX	H
99-93-129	8/93	ND	–	–
99-93-130	8/93	ND	–	–
541-7956	12/93	ND	–	–
541-7957	12/93	ND	–	–
541-7958	12/93	ND	–	–
541-7959	12/93	ND	–	–
541-4153	4/92	ND	–	–
541-4531	4/92	ND	–	–
541-4566	7/92	ND	–	–
541-4652	9/92	ND	–	–
SAF 3186	11/92	–	–	ND

^a Notation:

ND = not detected

– = not analyzed.

^b Detection limits are based on chemical agent in brine and are as follows:

GB, 2.0 ng/mL (nanograms/milliliter)

VX, 2.0 ng/mL

H, 200 ng/mL.

TABLE 3.18 CAMDS Performance Database^{a,b}

Chemical Laboratory Number	Chemical Laboratory Analysis Date	Reported Chemical Agent Concentration		
		GB	VX	H
51-98-01	1/98	ND	ND	ND
51-98-02	1/98	ND	ND	ND
51-98-03	1/98	ND	–	–
51-98-04	2/98	ND	–	ND
51-98-05	3/98	ND	–	–
51-98-06	3/98	ND	–	ND
51-98-07	3/98	ND	–	ND
51-98-08	4/98	ND	–	ND
51-98-09	4/98	ND	–	–
51-98-10	4/98	ND	–	–
51-98-11	5/98	ND	–	–
51-98-12	6/98	ND	–	–
51-98-13	7/98	ND	ND	–
51-98-14	7/98	ND	ND	–
16-98-12	8/98	ND	–	–
16-98-13	8/98	ND	–	–
16-98-14	8/98	ND	–	–
16-98-15	8/98	ND	–	–
51-98-15	9/98	ND	–	–

^a Notation:

ND = not detected

– = not analyzed.

^b Detection Limits are the based on chemical agent in brine and are as follows:

GB 2.0 ng/mL (nanograms/milliliter)

VX 2.0 ng/mL

H 200 ng/mL.

TABLE 3.19 TOCDF Performance Database^{a,b}

Chemical Laboratory Number	Chemical Laboratory Analysis Date	Reported Chemical Agent Concentration		
		GB	VX	H
8121.06	5/1/98	ND	-	-
8124.66	5/4/98	ND	-	-
8124.67	5/4/98	ND	-	-
8125.64	5/5/98	ND	-	-
8126.74	5/6/98	ND	-	-
8127.83	5/8/98	ND	-	-
8134.66	5/14/98	0.7 ppb	-	-
8134.67	5/14/98	0.7 ppb	-	-
8141.75	5/22/98	ND	-	-
8146.43	5/27/98	ND	-	-
8152.46	6/1/98	ND	-	-
8156.33	6/5/98	ND	-	-
8156.34	6/5/98	ND	-	-
8159.24	6/8/98	ND	-	-
8159.25	6/8/98	ND	-	-
8161.42	6/11/98	ND	-	-
8161.43	6/11/98	ND	-	-
8167.19	6/16/98	ND	-	-
8168.36	6/18/98	ND	-	-
6169.37	6/18/98	ND	-	-
8188.24	7/7/98	ND	-	-
8189.16	7/8/98	ND	-	-
8189.17	7/8/98	ND	-	-
8189.18	7/8/98	ND	-	-
8191.22	7/11/98	ND	-	-
8195.05	7/14/98	ND	-	-
8198.27	7/18/98	ND	-	-
8202.21	7/21/98	ND	-	-
8210.25	7/29/98	ND	-	-
8210.26	7/29/98	ND	-	-
8221.10	8/9/98	ND	-	-
8222.11	8/10/98	ND	-	-
8222.12	8/10/98	ND	-	-
8226.15	8/15/98	ND	-	-
8227.12	8/16/98	ND	-	-
8236.19	8/24/98	ND	-	-
8236.20	8/24/98	ND	-	-

TABLE 3.19 (Cont.)

Chemical Laboratory Number	Chemical Laboratory Analysis Date	Reported Chemical Agent Concentration		
		GB	VX	H
8243.02	8/31/98	ND	–	–
8251.16	9/9/98	ND	–	–
8251.17	9/9/98	ND	–	–

^a Notation:

ND = not detected

– = not analyzed

ppb = part per billion.

^b Detection limits are the based on chemical agent in brine and are as follows:

GB, 20.0 ng/mL (nanograms/milliliter)

VX, 20.0 ng/mL

H, 200 ng/mL.

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4 SUMMARY AND CONCLUSIONS

Table 4.1 summarizes the evaluation for each of the chemical agent neutralization procedures and concludes whether the chemical neutralization procedure is recommended as an LDR treatment technology. Tables 4.2 through 4.19 present summaries and conclusions for individual procedures on the basis of the evaluation categories presented in Section 3.1 and information from the performance databases presented in Section 3.2.

TABLE 4.1 Recommendation Summary

Chemical Neutralization Procedure	Applicable?	Demonstrated?	Recommended as LDR Treatment Technology?
Alkaline hydrolysis of GA	Yes	Yes	Yes
Alkaline hypochlorite neutralization of GA	Yes	Yes	Yes
Alkaline hydrolysis of GB	Yes	Yes	Yes
Alkaline hypochlorite neutralization of GB	Yes	Yes	Yes
Alkaline hydrolysis of GD	Yes	Yes	Yes
Alkaline hypochlorite neutralization of GD	Yes	Yes	Yes
Alkaline hydrolysis of GF	Yes	Yes	Yes
Alkaline hypochlorite neutralization of GF	Yes	Yes	Yes
Alkaline hydrolysis of VX	Not preferred	Yes	No
Alkaline hypochlorite neutralization of VX	Yes	Yes	Yes
Alkaline hydrolysis of Vx	Not preferred	No	No
Alkaline hypochlorite neutralization of Vx	Yes	No	Yes
Alkaline hypochlorite neutralization of H/HD	Yes	Yes	Yes
Alkaline hypochlorite neutralization of HT	Yes	No	Yes
Alkaline hypochlorite neutralization of HQ	Yes	No	Yes
Hypochlorite neutralization of HN1 and HN3	No	No	No
Alkaline hypochlorite neutralization of L	Yes	Yes	Yes
Alkaline hypochlorite neutralization of HL	Yes	No	Yes

TABLE 4.2 Alkaline Hydrolysis of GA

Evaluation Category	Comments
General chemistry and NMR data	Experimental evidence confirms the identity of the primary products of the alkaline hydrolysis of GA as Na[ethyl dimethylaminophosphonate] and NaCN. Products from the hydrolysis of the known impurity are present in low concentration.
Thermodynamics and kinetics	Thermodynamic considerations predict that the neutralization reaction proceeds to completion. Kinetic measurements confirm that the reaction is sufficiently rapid.
Re-formation of agent	Under conditions of alkaline hydrolysis in dilute solution, the re-formation of agent is not expected.
Performance database	The performance database contains five samples where this chemical neutralization procedure has been used at DPG in the past year.
Conclusions	Alkaline hydrolysis is applicable to the neutralization of GA, if the cyanide ion is kept below acceptable levels. Alkaline hydrolysis neutralization of GA has been demonstrated at DPG.

TABLE 4.3 Alkaline Hypochlorite Neutralization of GA

Evaluation Category	Comments
General chemistry and NMR data	The sodium salt of the phosphonate ion resulting from the alkaline hypochlorite neutralization of GA is the primary product of this reaction. The cyanide ion is destroyed by hypochlorite. This research did not confirm the fate of the dimethylamino group. Reaction products from the known impurity are present in low concentration. Excess hypochlorite can form chlorate upon standing.
Thermodynamics and kinetics	By comparison with GB, thermodynamic considerations suggest that for GA, the neutralization reaction proceeds to completion, and kinetic considerations suggest that the reaction is sufficiently rapid.
Re-formation of agent	Under the conditions of hypochlorite neutralization in dilute alkaline solution, cyanide ion is destroyed and the re-formation of agent is not possible.
Performance database	The performance database contains 12 samples where this chemical neutralization procedure has been used at DPG in the past year.
Conclusions	Hypochlorite neutralization is applicable to the neutralization of GA. Alkaline hypochlorite neutralization of GA has been demonstrated at DPG.

TABLE 4.4 Alkaline Hydrolysis of GB

Evaluation Category	Comments
General chemistry and NMR data	A large body of experimental evidence confirms the identity of the primary products of alkaline hydrolysis of GB as Na[IMPA] and NaF. Products from the hydrolysis of known additives and impurities are present in low concentration.
Thermodynamics and kinetics	Thermodynamic considerations predict that the neutralization reaction proceeds to completion. Kinetic measurements confirm that the reaction is sufficiently rapid.
Re-formation of agent	Under conditions of alkaline hydrolysis in dilute solution, the re-formation of agent is not expected.
Performance database	The performance database contains numerous samples where this chemical neutralization procedure has been used at DPG, DCD, CAMDS, and TOCDF.
Conclusions	Alkaline hydrolysis is applicable to the neutralization of GB. Alkaline hydrolysis neutralization of GB has been demonstrated at DPG, DCD, CAMDS, and TOCDF.

TABLE 4.5 Alkaline Hypochlorite Neutralization of GB

Evaluation Category	Comments
General chemistry and NMR data	Experimental evidence confirms the identity of the primary products of alkaline hypochlorite neutralization of GB to be the same as those from alkaline hydrolysis. Reaction products from the known impurities are present in low concentration. Reaction products from the known additives may include low concentrations of reversibly chlorinated ureas. Excess hypochlorite can form chlorate upon standing.
Thermodynamics and kinetics	Thermodynamic considerations suggest that the neutralization reaction proceeds to completion. Kinetic measurements confirm that the reaction is sufficiently rapid.
Re-formation of agent	Under the conditions of hypochlorite neutralization in dilute alkaline solution the re-formation of agent is not expected.
Performance database	The performance database contains seven samples where this chemical neutralization procedure has been used at DPG in the past year.
Conclusions	Hypochlorite neutralization is applicable to the neutralization of GB. Alkaline hypochlorite neutralization of GB has been demonstrated at DPG.

TABLE 4.6 Alkaline Hydrolysis of GD

Evaluation Category	Comments
General chemistry and NMR data	Experimental evidence confirms the primary products of alkaline hydrolysis of GD are Na[PMPA] and NaF. Products from the hydrolysis of known additives and impurities are present in low concentration.
Thermodynamics and kinetics	By comparison with GB, thermodynamic considerations suggest that the neutralization reaction proceeds to completion. Kinetic measurements confirm that the reaction is sufficiently rapid. An organic solvent may be added to the neutralization solution to increase the solubility of GD.
Re-formation of agent	Under conditions of alkaline hydrolysis in dilute solution, the re-formation of agent is not expected.
Performance database	The performance database contains six samples where this chemical neutralization procedure has been used at DPG in the past year.
Conclusions	Alkaline hydrolysis is applicable to the neutralization of GD. Alkaline hydrolysis neutralization of GD has been demonstrated at DPG.

TABLE 4.7 Alkaline Hypochlorite Neutralization of GD

Evaluation Category	Comments
General chemistry and NMR data	Experimental evidence confirms the identity of the primary products of alkaline hypochlorite neutralization of GD to be the same as those from alkaline hydrolysis, Na[PMPA] and NaF. Reaction products from the known impurities are present in low concentration. Excess hypochlorite can form chlorate upon standing.
Thermodynamics and kinetics	By comparison with GB, thermodynamic considerations suggest that the neutralization reaction for GD proceeds to completion, and kinetic considerations suggest that the reaction is sufficiently rapid. An organic solvent may be added to the neutralization solution to increase the solubility of GD.
Re-formation of agent	Under the conditions of hypochlorite neutralization in dilute alkaline solution, the re-formation of agent is not expected.
Performance database	The performance database contains 15 samples where this chemical neutralization procedure has been used at DPG in the past year.
Conclusions	Alkaline hypochlorite neutralization is applicable to the neutralization of GD and has been demonstrated at DPG.

TABLE 4.8 Alkaline Hydrolysis of GF

Evaluation Category	Comments
General chemistry and NMR data	Little experimental evidence was found regarding the products of the alkaline hydrolysis of GF. The products of hydrolysis of GF are expected to be similar to the products of hydrolysis of the related agents, GB and GD. The products of hydrolysis of probable additives and impurities are expected to be present in low concentrations.
Thermodynamics and kinetics	Thermodynamic considerations suggest that the neutralization reaction proceeds to completion. Kinetic considerations indicate that the reaction is sufficiently rapid. Allowance may need to be made (longer time for neutralization or use of an organic solvent) for the low solubility of GF in water.
Re-formation of agent	Under conditions of alkaline hydrolysis in dilute solution, the re-formation of chemical agent is not expected.
Performance database	The performance database contains seven samples where this chemical neutralization procedure has been used at DPG in the past year.
Conclusions	On the basis of the similarity of GF to GB and GD, alkaline hydrolysis is considered applicable to the neutralization of GF. Alkaline hydrolysis has been demonstrated at DPG.

TABLE 4.9 Alkaline Hypochlorite Neutralization of GF

Evaluation Category	Comments
General chemistry and NMR data	Little experimental evidence was found regarding the products of the neutralization of GF in alkaline hypochlorite. By comparison with the reactions of the related agents, GB and GD, the products of hydrolysis of GF are expected to be similarly innocuous. Products of hydrolysis of probable additives and impurities are present in low concentrations. Excess hypochlorite can form chlorate upon standing.
Thermodynamics and kinetics	By comparison with GB, thermodynamic considerations suggest that the neutralization reaction proceeds to completion, and kinetic considerations suggest that the reaction is sufficiently rapid. Allowance may need to be made (longer time for neutralization or use of an organic solvent) for the low solubility of GF in water.
Re-formation of agent	Under the conditions of hypochlorite neutralization in dilute alkaline solution, the re-formation of agent is not expected.
Performance database	The performance database contains 11 samples where this chemical neutralization procedure has been used at DPG in the past year.
Conclusions	Hypochlorite neutralization is applicable to the neutralization of GF. Alkaline hypochlorite neutralization of GF has been demonstrated at DPG.

TABLE 4.10 Alkaline Hydrolysis of VX

Evaluation Category	Comments
General chemistry and NMR data	There is convincing evidence that the principal products of the alkaline hydrolysis of VX are the sodium salt of ethyl methylphosphonic acid, DESH, and EA 2192. DESH can be air oxidized to EA 4196. Products from the hydrolysis of known additives and impurities are present in low concentration.
Thermodynamics and kinetics	Thermodynamic considerations suggest that the neutralization reaction proceeds to completion. Kinetic considerations indicate that the reaction is sufficiently rapid.
Re-formation of agent	Under conditions of alkaline hydrolysis in dilute solution the re-formation of VX is not expected.
Performance database	The performance database contains eight samples where this chemical neutralization procedure has been used at DPG in the past year.
Conclusions	Because the possible formation of EA2192, alkaline hydrolysis is not the preferred neutralization procedure for VX.

TABLE 4.11 Alkaline Hypochlorite Neutralization of VX

Evaluation Category	Comments
General chemistry and NMR data	The neutralization reaction of VX in alkaline hypochlorite has not been characterized completely. Reaction products from the known impurities are present in low concentration. Reaction products from the known additives may include low concentrations of reversibly chlorinated ureas. Excess hypochlorite can form chlorate upon standing.
Thermodynamics and kinetics	Thermodynamic considerations predict that the neutralization reaction proceeds to completion. Kinetic measurements confirm that the reaction is sufficiently rapid.
Re-formation of agent	Under the conditions of hypochlorite neutralization in dilute alkaline solution, the re-formation of VX is not possible.
Performance database	The performance database contains numerous samples where this chemical neutralization procedure has been used at DPG, DCD, and CAMDS.
Conclusions	Alkaline hypochlorite neutralization is applicable to the neutralization of VX. Alkaline hypochlorite neutralization of VX has been demonstrated at DPG, DCD, and CAMDS.

TABLE 4.12 Alkaline Hydrolysis of Vx

Evaluation Category	Comments
General chemistry and NMR data	By comparison to VX, it is expected that the principal products of the alkaline hydrolysis of Vx are the sodium salt of iso-butyl methylphosphonic acid and the Vx analogs of DESH and EA 2192. The Vx analog of DESH may be air oxidized to the Vx analog of EA 4196. Products from the hydrolysis of known additives and impurities are expected to be present in low concentration.
Thermodynamics and kinetics	By comparison to VX, thermodynamic considerations suggest that the neutralization reaction proceeds to completion. Similar kinetic considerations indicate that the reaction is sufficiently rapid.
Re-formation of agent	Under conditions of alkaline hydrolysis in dilute solution the re-formation of Vx is not expected.
Performance database	The performance database contains no evidence that this chemical neutralization procedure has been used at DPG in the past year.
Conclusions	Because of the possible formation of the Vx analogs of EA2192 and EA4196, alkaline hydrolysis is not the preferred neutralization procedure for Vx.

TABLE 4.13 Alkaline Hypochlorite Neutralization of Vx

Evaluation Category	Comments
General chemistry and NMR data	The neutralization reaction of Vx in alkaline hypochlorite has not been characterized. Reaction products from the known impurities are present in low concentration. Reaction products from the known additives may include low concentrations of reversibly chlorinated ureas. Excess hypochlorite can form chlorate upon standing.
Thermodynamics and kinetics	By comparison with VX, thermodynamic considerations predict that the neutralization reaction proceeds to completion, and comparable kinetic measurements suggest that the reaction is sufficiently rapid.
Re-formation of agent	Under the conditions of hypochlorite neutralization in dilute alkaline solution, the re-formation of Vx is not expected.
Performance database	The performance database contains no evidence that this chemical neutralization procedure has been used at DPG in the past year.
Conclusions	On the basis of similarity of Vx to VX, alkaline hypochlorite neutralization is expected to be applicable to the neutralization of Vx. Alkaline hypochlorite neutralization of Vx has not been demonstrated at DPG; however, results are expected to be similar to results for VX.

TABLE 4.14 Alkaline Hypochlorite Neutralization of H/HD

Evaluation Category	Comments
General chemistry and NMR data	In the presence of excess neutralization solution, at high pH, and with adequate stirring, alkaline hypochlorite will oxidize HD to sulfate, chloride, and carbonate. A variety of uncharacterized compounds remain at low concentration after neutralization. Impurities probably are oxidized in a similar manner.
Thermodynamics and kinetics	Thermodynamic considerations predict that the neutralization reaction proceeds to completion. Kinetic data were not found.
Re-formation of agent	Under the conditions of hypochlorite neutralization in dilute alkaline solution, the re-formation of HD is not possible. Allowance may need to be made (longer time for neutralization or use of an organic solvent) for the low solubility of HD in water.
Performance database	The performance database contains numerous samples where this chemical neutralization procedure has been used at DPG, DCD, and CAMDS.
Conclusions	Alkaline hypochlorite is applicable to the neutralization of HD. Alkaline hypochlorite neutralization of HD has been demonstrated at DPG, DCD, and CAMDS.

TABLE 4.15 Alkaline Hypochlorite Neutralization of HT

Evaluation Category	Comments
General chemistry and NMR data	The neutralization of HT in alkaline hypochlorite has not been characterized. Agent T is very similar to HD and is expected to give the same products as HD in the alkaline hypochlorite neutralization.
Thermodynamics and kinetics	Thermodynamic and kinetic data were not found. On the basis of the similarity of T to HD, the reaction is expected to proceed in the same way. Additional allowance may need to be made (longer time for neutralization or use of an organic solvent) for the low solubility of T in water.
Re-formation of agent	Under the conditions of hypochlorite neutralization in dilute alkaline solution, the re-formation of HD or T is not expected.
Performance database	The performance database contains no evidence that this chemical neutralization procedure has been used at DPG, DCD, or CAMDS.
Conclusions	On the basis of similarity of HT to HD, alkaline hypochlorite is applicable to the neutralization of HT. Alkaline hypochlorite neutralization of HT has not been demonstrated; however, results are expected to be similar to results for HD.

TABLE 4.16 Alkaline Hypochlorite Neutralization of HQ

Evaluation Category	Comments
General chemistry and NMR data	The neutralization of HQ in alkaline hypochlorite has not been characterized. Agent Q is very similar to HD and is expected to give the same products as HD in the alkaline hypochlorite neutralization.
Thermodynamics and kinetics	Thermodynamic and kinetic data were not found. On the basis of the similarity of Q to HD, the reaction is expected to proceed in the same way. Additional allowance may need to be made (longer time for neutralization or use of an organic solvent) for the low solubility of Q in water.
Re-formation of agent	Under the conditions of hypochlorite neutralization in dilute alkaline solution, the re-formation of HD or Q is not expected.
Performance database	The performance database contains no evidence that this chemical neutralization procedure has been used at DPG in the past year.
Conclusions	On the basis of similarity of HQ to HD, alkaline hypochlorite is applicable to the neutralization of HQ. Alkaline hypochlorite neutralization of HQ has not been demonstrated at DPG; however, results are expected to be similar to results for HD.

TABLE 4.17 Hypochlorite Neutralization of HN1 and HN3

Evaluation Category	Comments
General chemistry and NMR data	No experimental evidence was found to support the applicability of hypochlorite neutralization to HN1 and HN3.
Thermodynamics and kinetics	No thermodynamic or kinetic data were found.
Re-formation of agent	No information regarding the re-formation of HN1 and HN3 from neutralization solutions was found.
Performance database	The performance database contains no evidence that this chemical neutralization procedure has been used at DPG in the past year.
Conclusions	Consider hypochlorite neutralization not applicable to HN1 or HN3 until supporting information is found. Hypochlorite neutralization of HN1 or HN3 has not been demonstrated at DPG.

TABLE 4.18 Alkaline Hypochlorite Neutralization of L

Evaluation Category	Comments
General chemistry and NMR data	L1 and its isomers are converted to acetylene, arsenite, and chloride in the presence of base. In the presence of alkaline hypochlorite, the arsenite is converted to arsenate. L2 and L3 are expected to form the same products. A trace of geminal L, if present, forms vinyl chloride, arsenate, and chloride.
Thermodynamics and kinetics	Thermodynamic considerations predict that the neutralization reaction proceeds to completion. Kinetic measurements confirm that the reaction is sufficiently rapid. Allowance may need to be made (longer time for neutralization or use of an organic solvent) for the low solubility of L in water.
Re-formation of agent	Under the conditions of hypochlorite neutralization in dilute alkaline solution, acetylene is formed and the re-formation of the L is not possible.
Performance database	The performance database contains five samples where this chemical neutralization procedure has been used at DPG in the past year.
Conclusions	Alkaline hypochlorite is applicable to the neutralization of L. Alkaline hypochlorite neutralization of L has been demonstrated at DPG. CAMDS is also presently proceeding with a RD&D permit for neutralization of L using the Chem-Security process, as discussed in Section 2.2.

TABLE 4.19 Alkaline Hypochlorite Neutralization of HL

Evaluation Category	Comments
General chemistry and NMR data	The neutralization of HL in alkaline hypochlorite has not been characterized. The reaction is expected to proceed as parallel HD and L neutralizations.
Thermodynamics and kinetics	Thermodynamic considerations suggest that the neutralization reactions would proceed to completion. Kinetic considerations suggest that the reaction is sufficiently rapid. Allowance may need to be made (longer time for neutralization or use of an organic solvent) for the low solubility of HD and L in water.
Re-formation of agent	Under the conditions of hypochlorite neutralization in dilute alkaline solution, re-formation of the agents is not expected.
Performance database	The performance database contains no evidence that this chemical neutralization procedure has been used at DPG in the past year.
Conclusions	On the basis of similarity of HL to HD and L, alkaline hypochlorite is applicable to the neutralization of HL. Although alkaline hypochlorite neutralization of HL has not been demonstrated at DPG, results are expected to be similar to those for HD and L.

5 REFERENCES

AGEISS Environmental, Inc. (AGEISS), 1998, *Background Document For Chemical Neutralization as a Land Disposal Restriction Treatment Technology For Chemical Agent Associated Waste*, prepared for the Directorate of Environmental Programs, U.S. Army Dugway Proving Ground, Dugway, Utah (July 24).

Beaudry, W.T., et al., 1993, *Analysis of Decontamination Solutions of G Agents to Detect Reformation of Agent*, ERDEC-TR-005, Research and Technology Directorate, Edgewood Research, Development, and Engineering Center, Md. (Jan.).

ChemFinder.com (Internet searching and information).

Davis, G.T., et al., 1977, *Fundamental Studies Related to the Decontamination and Disposal of GB-Filled Honest John Warhead Components*, EC-TR-76101, U.S. Army Chemical Systems Laboratory, Aberdeen Proving Ground, Md. (March).

Davis, P.M., et al., 1979, *Decontaminating Solution for the Disposal of Identification and Training Sets*, Army Armament Research and Development Command, Aberdeen Proving Ground, Md. (April).

Departments of the Army, Navy, and Air Force, 1990, *Potential Military Chemical/Biological Agents and Compounds*, Field Manual 3-9, Washington, D.C.

Dugway Proving Ground, 1978, *Operation Plan, Range Clearance of Dugway Proving Ground Hazardous Areas; Appendix B: Description of Agents*, Dugway, Utah (March).

Durst, H.D., et al., 1988, *Support for the Delisting of Decontaminated Liquid Chemical Surety Materials as Listed Hazardous Waste from Specific Sources*, CRDEC-TR-009, Research Directorate, Chemical Research, Development, and Engineering Center, Aberdeen Proving Ground, Md. (Nov.).

Edgewood Arsenal, 1974, *Chemical Agent Data Sheets*, Special Report EO-SR-74001, Vol. 1, Headquarters, Edgewood Arsenal, Aberdeen Proving Ground, Md. (Dec.).

Field Manual 3-9: See Departments of the Army, Navy, and Air Force.

Hewitt, C.L., 1948, "Isomers of 2-Chlorovinylchloroarsine," *J. Chem. Soc.* 1203-1205.

Jackson, K.E., and M.A. Jackson, 1935, "The Chlorovinylarsines," *Chem.* 16:429-452.

Jody, B.J., et al., 1983, *Development of Chemical Processes for Chemical Demilitarization — Phase I*, DRXTH-TE-CR-83209, prepared for U.S. Army Toxic and Hazardous Materials Agency, Aberdeen Proving Ground, Md., by IIT Research Institute, Chicago, Ill.

MacNaughton, M.G., and J.H. Brewer, 1994, *Environmental Chemistry and Fate of Chemical Warfare Agents*, Final Report SWRI 01-5864, prepared for U.S. Army Corps of Engineers by Southwest Research Institute, San Antonio, Texas.

Mcandless, J.M., and V. Fedor, 1992, *Destruction and Waste Treatment Methods Used in a Chemical Agent Disposal Project*, Defence Research Establishment, Suffield Ralston, Alberta, Canada (Oct.).

Rosenblatt, D.H., et al., 1995, *Agent/Decontamination Chemistry Technical Report*, U.S. Army Test and Evaluation Command (Oct.).

Rosenblatt, D.H., et al., 1975, *Problem Definition Studies on Potential Environmental Pollutants*, Technical Report 7509, U.S. Army Medical Bioengineering Research and Development Center, Fort Detrick, Md.

Safety Office, 1995, "Material Safety Data Sheet for HQ," U.S. Army Chemical, Research, Development, and Engineering Center, Aberdeen Proving Ground, Md. (June).

Samuel, J.B., et al., 1983, *Physical Properties of Standard Agents, Candidate Agents, and Related Compounds at Several Temperatures (U)*, Special Publication ARCSL-SP, Chemical Systems Laboratory, Aberdeen Proving Ground, Md. (June).

Samuel, J.B., et al., 1998, *Agent Neutralization Study II: Detoxification of HD with Aqueous Bleach*, ERDCE-TR-458, Research and Technology Directorate (Jan.).

Smith, J.R., et al., 1993, "Identification of the Isomeric Forms of Lewisite Using Mass Spectrometry, NMR and IR Spectroscopy, and Molecular Modeling," pp. 351-360 in *1993 Medical Defense Biosciences Review Proceedings*, Volume 1, U.S. Army Medical Research and Development Command (May).

U.S. Army, 1999, *A Technical Evaluation Derivation of Health-Based Environmental Screening Levels for Chemical Warfare Agents*, Draft, U.S. Army Center for Health Promotion and Preventive Medicine, Aberdeen Proving Ground, Md. (Feb.)

U.S. Army Medical Research Institute of Chemical Defense, 1995, *Medical Management of Chemical Casualties Handbook* (2nd ed.), Chemical Casualty Care Office, Aberdeen Proving Ground, Md. (Sept.).

Waters, W.A., and J.H. Williams, 1950, "Hydrolyses and Derivatives of Some Vesicant Arsenicals" *J. Chem. Soc.* 18-22.

Yang, Y.-C., et al., 1992, "Decontamination of Chemical Warfare Agents," *Chem. Rev.* 92:1729-1743.

Yurow, H.W., and G.T. Davis, 1982, *Decontamination and Disposal Methods for Chemical Agents - A Literature Survey*, ARCSL-TR-81080, U.S. Army Armament Research and Development Command, Aberdeen Proving Ground, Md. (Nov.).

Yurow, H.W., 1988, *Decontamination of Chemical Agents GA, GB, GD, HD, L, and VX - A Literature Survey (1918-1987)*, CRDEC-SP-88020, Chemical Research, Development, and Engineering Center, Aberdeen Proving Ground, Md. (Nov.).

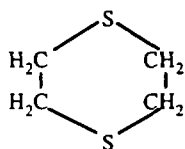
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APPENDIX A:
CHEMICAL STRUCTURES DICTIONARY

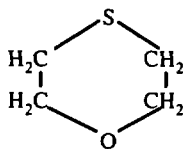
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**APPENDIX A:
CHEMICAL STRUCTURES DICTIONARY**

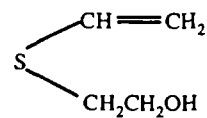
Appendix A presents a chemical structures dictionary for the chemicals discussed in the report.



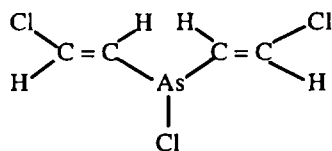
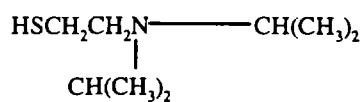
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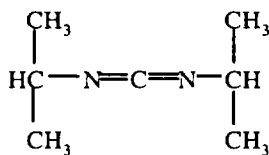
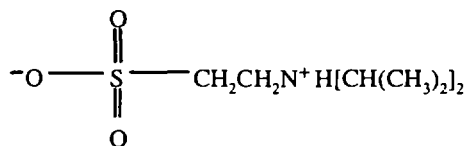
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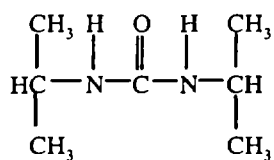
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bis-(2-chlorovinyl) chloro arsine
or L2

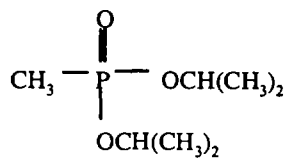
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N,N'-Diisopropyl
Carbodiimide

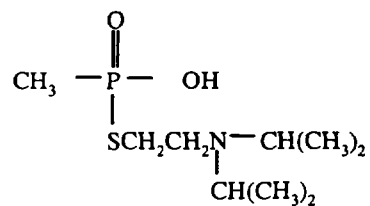
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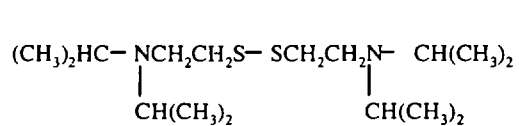
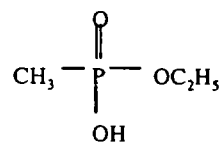
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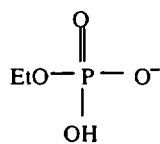
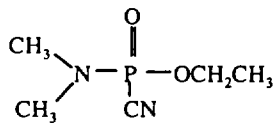
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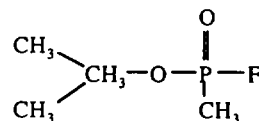
EA 2192

EA4196 OR (DES)₂

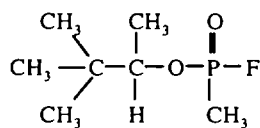
EMPA

Ethyl ester of phosphonic acid,
anion form

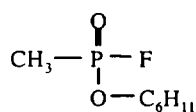
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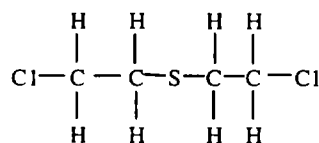
GB



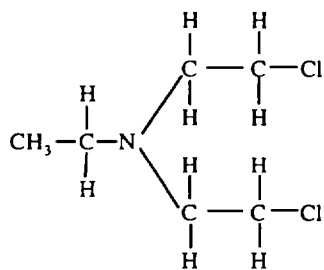
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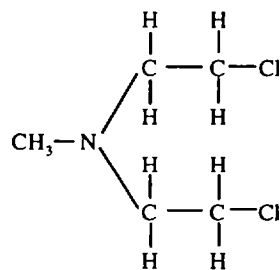
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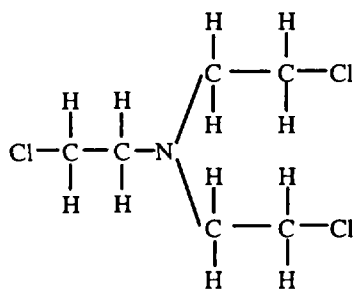
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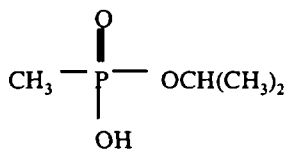
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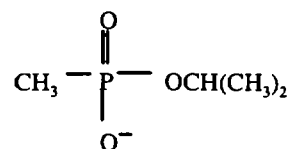
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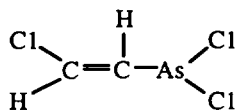
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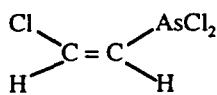
IMPA



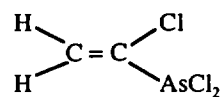
IMPA Anion



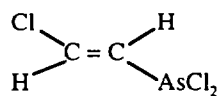
L



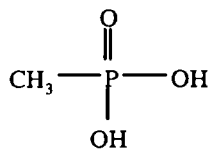
cis-Lewisite



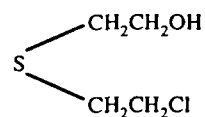
geminal-Lewisite



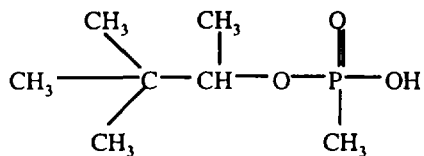
trans-Lewisite



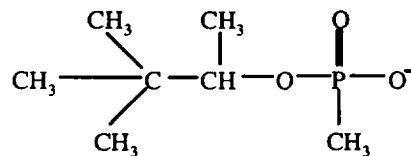
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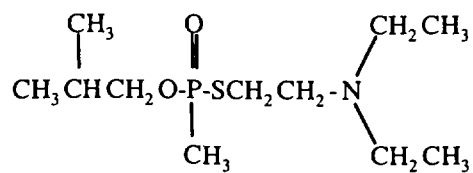
Mustard Chlorohydrin



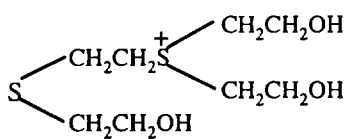
Pinacolylmethyl phosphonic acid



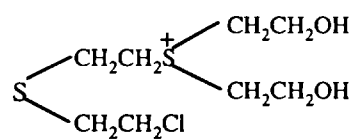
Pinacolylmethyl phosphonic acid anion



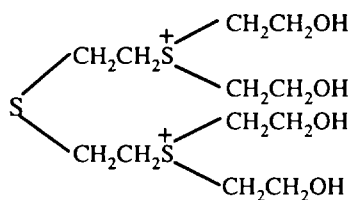
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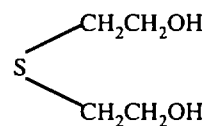
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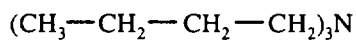
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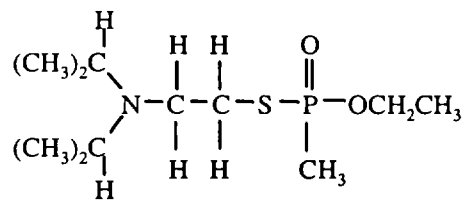
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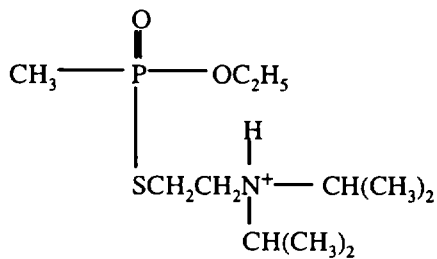
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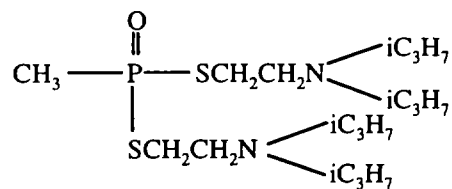
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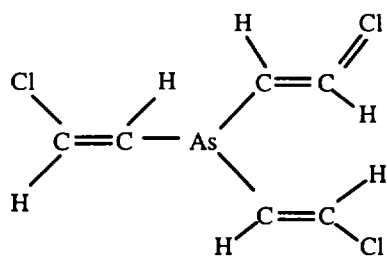
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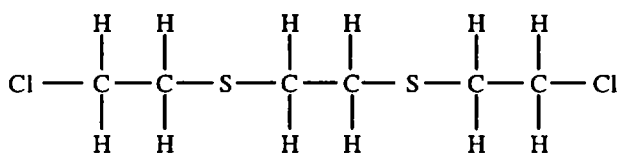
Protonated VX



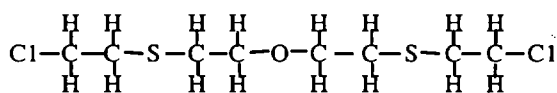
"Bis Impurity" in VX



L-3 or Tris(2-chlorovinyl)arsine



Q



T